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A Novel Process for Demulsification of Water-in-Crude Oil Emulsions by Dense Carbon Dioxide

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CO_2 was used to break several water-in-crude oil and water-in-model oil emulsions stabilized by asphaltenic films. The stability of asphaltenic films in model oils having varying H/C ratios (aromaticities) was also studied upon contact with liquid or supercritical CO_2. The efficacy and kinetics of demulsification appeared to be enhanced with increased CO_2 density and mole fraction. The proposed mechanism by which CO_2 destabilizes water-in-crude oil emulsions involves asphaltene flocculation and precipitation. The emulsions break by flocculating the adsorbed asphaltenes, leading to film defects, film thinning, film rupture, and water coalescence. The various factors influencing asphaltene precipitation and emulsion destabilization were studied in model solvent systems containing asphaltenes and resins. Increasing CO_2 pressure, residence time, temperature, and degree of mixing were found to increase the rate of asphaltene precipitation. Asphaltene precipitation by CO_2 was found to increase in the presence of water as compared to precipitation from water-free systems. It is apparent that CO_2 preferentially precipitates the most surface-active portion of asphaltenes, leading to a substantial weakening of the viscoelastic asphaltenic film built around the dispersed water droplets in the emulsion. The rate of the demulsification process was greatly enhanced when the emulsion was injected under pressure into compressed CO_2 as a result of the enhanced CO_2/emulsion volume ratio and mass transfer rates.

Introduction

This work describes the use of dense CO_2 to destabilize water-in-crude oil and water-in-model oil emulsions stabilized by asphaltenic films. CO_2 acts by flocculating and precipitating the asphaltenes at the interface, leading to interfacial defects, film thinning, film rupture, and droplet coalescence. The stability of many water-in-oil (w/o) emulsions is known to arise from the formation of elastic asphaltenic films at the oil–water interface.[1–7] Asphaltenes are the *n*-heptane or *n*-pentane insoluble fraction of crude oil and consist of sheets of condensed aromatic rings combined with short aliphatic chains and naphthenic rings.[8,9] Apart from carbon and hydrogen, small amounts of nitrogen, oxygen, sulfur, and metals (particularly, iron, vanadium, and nickel) are present.[10] Both hydrogen bonding and polar interactions between asphaltene molecules contribute to the film elasticity and strength observed.

Asphaltenes form the most stable emulsions of w/o, at their limits of solubility, i.e., a condition of incipient precipitation.[11–13] A primary adsorbed layer is initially formed, almost certainly comprised of asphaltenes, and a secondary layer superimposes on this primary layer and is likely comprised of asphaltenes, wax particles, and possibly inorganic particulates.

Currently, asphaltenic emulsions are typically destabilized through the use of chemical demulsifiers.[14–16] The chemical structure of these demulsifiers is usually based on alkylphenol formaldehyde ethoxylated resins. These chemical demulsifiers are effective, but, unfortunately, these chemicals are now believed to be endo-

crine disrupters, and thus it is likely that they may be banned by various national environmental protection agencies. Additionally, these materials are very costly, and they need to be tailored chemically or formulated for different types of crude oil emulsions. Other means of destabilizing asphaltene-stabilized w/o emulsions include thermal pressurization and rapid depressurization,[17] and electrostatic droplet shattering and coalescence.[18,19] Both of these methods are established around efforts at "cracking" or "disrupting" the rigid, viscoelastic film of asphaltenes that forms around the water droplets. One problem with these methods is the reforming of stabilized water droplets due to readsorption of displaced or "disrupted" asphaltenic film fragments in shear fields under solvent conditions at which the asphaltenes are capable of reassembly.

The use of CO_2 in breaking oil-in-water (o/w) emulsions was described by Little et al.[20,21] This process is similar to air flotation; the flocculation of the dispersed oil droplets is the result of two separate effects: a pH effect due to the acidity of CO_2 and a flotation/coalescence effect due to the rising CO_2 bubbles. CO_2 causes a decrease in the aqueous phase pH, which lowers the electrostatic charge on the surface of the oil droplets (the abundance of carboxylic acid functional groups in crude oil typically renders crude oil droplets in water negatively charged). However, this method is not applicable to the demulsification of w/o emulsions, which have higher viscosities than o/w and are not responsive to gas flotation.

Recently, Sjoblom, Auflem, and co-workers[22–24] have described a process for the separation of oil, water, and gas during the production and processing of petroleum fluids in which carbon dioxide (and comparable gases) is introduced at elevated pressure into a separator, along with water and oil (the oil phase typically com-

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Table 1. Physicochemical Properties of Crude Oils

crude	API gravity	density g/cm^3 @ 60°F	dynamic viscosity cP @ 100 °F	asphaltene content (wt %)	resin content (wt %)	critical electric fields of 30 v/v% water-in-crude oil emulsions (kV/cm)
Arab Berri	37.3	0.83827	4.39	0.79	3.24	0.26
Hondo	19.4	0.93771	363	14.81	20.52	2.88
B6	19.8	0.93523	2030	13.11	12.04	1.71

prised of a w/o emulsion). As the pressure is reduced, bubbles of the carbon dioxide will form by nucleation from solution and will coalesce to form sufficiently large bubbles to induce flotation. According to the invention,[23] the bubbles tear off the asphaltenes and natural crude oil surfactants as they pass from the water to oil phase and through the oil phase. This method is complementary to Little's method described above.

Hydrocarbon gases have been used in deasphalting crude oils for the production of lubricating oils.[25] Butane or propane at 50 °C dissolves all the constituents of a lube-oil feedstock except for the asphalt. Because the propane−lube oil mixture possesses a low viscosity, the asphalt fraction is readily separated from the mixture and is easily recovered. The refrigerant properties of liquid propane are exploited so that the waxes are precipitated from the mixture by reducing pressure, which upon evaporation of a small portion of the solution, causes the temperature of the mixture to decrease to approximately 40 °C. Heating the remaining propane−oil mixture to temperatures near 100 °C decreases the solvent power of liquid propane, resulting in the sequential precipitation of the resins, the heavy ends, and the naphthenic constituents, thus leaving only the lightest paraffins in solution. The residuum oil supercritical extraction (ROSE) process was developed by Kerr McGee in the 1970s.[26] The first stage of the ROSE process consists of mixing residuum with compressed liquid butane or pentane and precipitating the undesired asphaltene fraction. This step is similar in sequencing to the previously described propane-deasphalting process. The reason butane is used, incidentally, is that it has a higher solvent power for the heavy hydrocarbons. Hence, for the higher molecular weight resid, butane is an effective solvent in dissolving the desired high molecular weight components and precipitating the asphaltenes.

In what follows, we describe the first use of dense CO_2 to demulsify water-in-crude oil and water-in-model oil emulsions stabilized by asphaltenic films. The presumed mechanism is the flocculation and precipitation of the asphaltenes at the interface, which leads to interfacial defects and desorption, film thinning, film rupture, and droplet coalescence. The effects of temperature and pressure on the CO_2-demulsification of both water-in-crude oil and water-in-model oil emulsions are investigated. Different factors affecting asphaltene precipitation and fractionation from model oils with dense CO_2 are discussed. The factors influencing the kinetics of demulsification with CO_2 are studied with the aim of accelerating the demulsification process.

Experimental Section

Materials. The crude oils chosen for this study (Arab Berri, Hondo, and B6) were selected because of their extensive use in oil refineries and because they represent extremes in gravity, resin, and asphaltene contents, and emulsion-forming tendencies. The general proper-

ties of the crude oils selected for this study are presented in Table 1. All solvents were HPLC grade supplied from Fischer Scientific, water was deionized water, and CO_2 was a Coleman grade with 99.99% purity.

Methods. (a) Model Oils. Model oils were prepared by mixing asphaltenes with various ratios of heptane and toluene. Asphaltenes were first precipitated from Hondo crude oil by *n*-heptane addition (40:1 *n*-heptane/ crude oil). Asphaltenes were weighed to the nearest 0.1 mg in a 15-mL polypropylene (PP) vial, and to them the prerequisite volume of toluene was added. The vial was capped and was shaken for 1 h to ensure complete solubility of asphaltenes. The prerequisite volume of *n*-heptane was added, and again the vial was capped and it was shaken for 1 h. The percentage weight of asphaltenes in the heptane−toluene mixture was 3 wt %. The ratios of heptane to toluene were varied, namely, 50:50, 60:40, and 70:30, respectively.

(b) Crude Oils. To ensure homogeneity of the oil samples, the whole crudes were mixed thoroughly with the use of a Harbil GQM high-speed paint mixer for 3 min.

(c) Emulsions. Crude oil and model oil emulsions were prepared by mixing crude oil or model oil with deionized water. Six milliliters of deionized water, pH adjusted at 6 and containing 1% NaCl, was added to 4 mL of model oil or crude oil in a glass vial. The mixture was emulsified using an ultrahigh speed Virtishear Cyclone IQ homogenizer with a 6-mm rotor/stator configuration (gap width 0.127 mm) at 15 000 rpm for 2 min at the oil−water interface and for 1 min at the bottom of the vial. Immediately after emulsification, the emulsion was transferred to 20-mL glass tubes capped with poly(tetrafluoroethylene) (PTFE) lined lids. The emulsion was left for 24 h before it was demulsified by CO_2. Because of the high stability of the prepared emulsions, no water separation was observed after the 24 h period. The amounts of oil and water to be emulsified (including the w/o ratio), the geometry of emulsifying equipment (e.g., 15-mL jar, 6-mm rotor/ stator configuration), and the amount of energy input to the system specified in the emulsification protocol were determined in preliminary experiments to ensure reproducibility, complete emulsification of materials, and droplet size distributions typical of emulsions produced in the production and refining of petroleum (1−15 μm). Emulsion stability was gauged by two methods: by the critical electric field method[40] and by centrifugal resolution of water (the dispersed phase).

Demulsification Experiments. (a) Emulsion Pressurization with CO_2. The prepared emulsions were transferred to a 20-mL cylindrical stainless steel high-pressure cell supplied with two sapphire windows (Figure 1). The cell has an inlet gas valve, an outlet gas valve supplied by HIP-industries connected to a pressure rupture disk, and a pressure transducer (model OMEGA PX302-1OKGV), which is connected to a pressure readout (model OMEGA DP25-S). Heating was maintained using a thermal-tape and the temperature
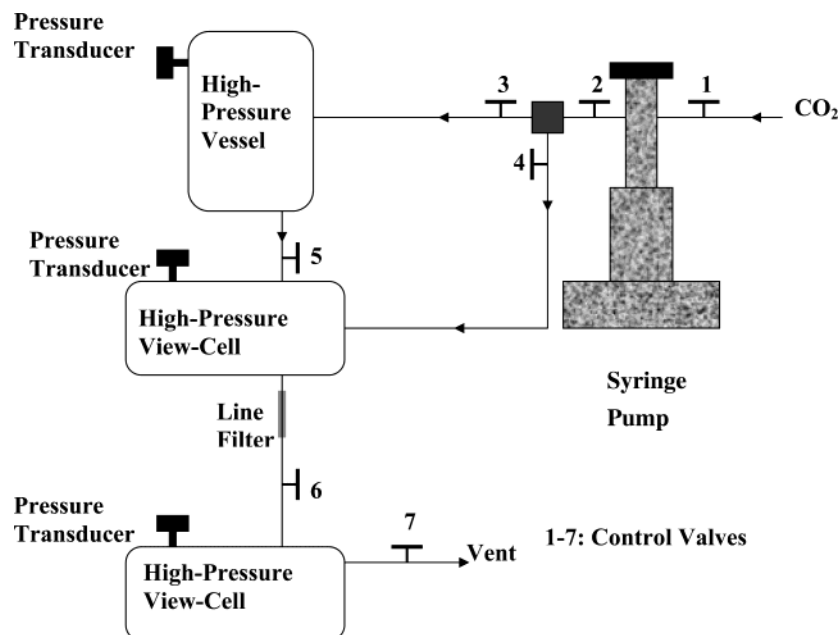
Figure 1. Experimental setup for high-pressure injection of emulsion into CO_2 and resulting asphaltene precipitation and demulsification.

was probed by a K-type (Chrom-Alumel) thermocouple connected to a temperature controller model CN 773 53-A2. A schematic representation of the cell and the system is illustrated in Figure 1. The system was heated to the desired temperature (25–70 °C) at a constant heating rate of 2 °C/min. When the desired temperature was reached, CO_2 was conveyed to the system by means of a digital syringe pump model ISCO 260D at a low pressure to remove air from the system. CO_2 was then pumped continuously until the desired initial pressure was reached. The system was left at this temperature and water separation was observed through the sapphire window every hour for the first 6 h and then after 24 h. At the end of the 24 h period, the system was cooled to ambient temperature, and then CO_2 was depressurized at a steady rate of 2 mL/min to avoid foaming. The cell was opened, and the separated water (if any) was removed by a syringe and placed into a graduated cylinder for quantification.

(b) Demulsification Kinetics of Water-in-Model Oil Emulsions. Emulsions composed of 60 vol/vol % water and 40 vol/vol % model oil were prepared as described before. The model oil was composed of 45 vol % heptane and 55 vol % toluene containing 1 wt/vol % B6 asphaltenes. Five milliliters of the emulsion was charged in a 20-mL capacity high-pressure view-cell, heated to the desired temperature (ranging from 25 to 100 °C), and pressurized with CO_2 at 2000 psi fixed pressure. The system was kept at these conditions for the required period of time, namely, 30, 60, 120 min, after which the CO_2 was discharged slowly, and the system was allowed to cool to ambient temperature. The cell was opened and the separated water was quantified by phase separating the aqueous phase from the oil phase. The retrieved water was quantified by discharging it into a graduated cylinder. For each studied temperature, three experiments were made at 30, 60, and 120 min.

(c) Emulsion Injection in Dense CO_2 under Pressure. To accelerate the rate of the demulsification process, the prepared emulsions were injected in liquid or supercritical CO_2. The system used for executing these experiments is depicted in Figure 1. In this system, a 20-mL capacity high-pressure stainless steel contactor containing the emulsion is connected to two high-pressure view cells with the same specifications described above. CO_2 is delivered at a specified pressure and flow rate from the syringe pump through a three-way valve (3) to the first view cell to fill it with liquid CO_2. The syringe pump is set to deliver CO_2 at a higher pressure through the three-way valve (3), which is switched to fill the high-pressure contactor already containing the water-in-crude oil emulsion. The temperature was controlled in the contactor and the two view cells by means of a thermal-tape, and the temperature was probed by a K-type (Chrom-Alumel) thermocouple connected to a temperature controller model CN 773 53-A2. The contents of the high-pressure reactor were forced under pressure to the first view cell and the flow rate was controlled by valve (5). In the first view cell, water separation was observed visually through the sapphire windows of the cell. When the process went to completion, the drain valve (6) was opened to force the separated water into the second view cell. The separated water collected in the second view cell was quantified by discharging it into a graduated cylinder.

Quantifying Precipitated Asphaltenes and Resins. The amount of precipitated asphaltenes and/or resins was determined quantitatively. The experimental setup depicted in Figure 1 was used for the determination of the amount precipitated. Accurately weighed (to the nearest 0.1 mg) B6 asphaltenes or B6 resins were dissolved in 10 mL of toluene to make a 1 wt/vol % solution. The solution was delivered quantitatively to the view cell, pressurized with CO_2 by means of the syringe pump to the desired pressure (1000–2000 psia). If stirring was to be employed in the experiment, a magnetic stirring bar was placed in the system, and the view cell was mounted on a magnetic stirrer adjusted to 500 rpm. The system was left for the desired period of time after which the solvent was conveyed under CO_2 pressure through a 1.5 μm line filter to a collecting cell. The system was flushed with CO_2 several times. The system was depressurized from CO_2 and the precipitated fraction left in the view cell was recovered by dissolution in methylene chloride. Likewise, the dis-

solved fraction located in the collecting cell was recovered by dissolution in methylene chloride. Both fractions were collected in tared glass bottles and placed in a vacuum oven to evaporate the solvent until the mass remained constant. The masses of both the precipitated and dissolved fractions were determined and the % precipitated and soluble fractions were calculated.

^{1}H NMR Spectroscopy. The asphaltene samples were dissolved in $CDCl_3$ and analyzed in a 300 MHz General Electric NMR spectrometer.

Molecular Weight Determination by Vapor Pressure Osmometry. A Knauer vapor pressure osmometer was used to determine the number average molecular weight. The asphaltene samples were dissolved in chlorobenzene and analyzed at 90 °C. Acetanilide was used to calibrate the instrument.

Elemental Analysis. A Leco Elemental Analyzer model 1000 was used to determine the CHNS and O content of different asphaltene fractions. A combustion aid (V_2O_5 powder) was added to ensure complete combustion of the hard-to-combust asphaltene samples.

Critical Electric Field Measurement. The stability of the water-in-crude oil emulsions was gauged with critical electric field (cef) measurements.[24] To measure cef, an emulsion sample was placed in the sample cell (in a 60 °C oven) consisting of two 1.0-cm diameter, gold plated, copper electrodes, separated with Mylar spacers, and held in an aluminum casing. The cell was designed so the gap width could be varied, but for all of the experiments it was 0.25 mm. Two holes were drilled through the top for sample introduction. A syringe was used to withdraw a sample from the middle of the emulsion and inject it through one of the holes in the cell. The cell was connected to a HP6634B power supply (0−100 V DC source), controlled by a PC through the use of a HP82350A interface card. Using this card, the power supply was controlled with a Visual Basic program.

After the sample was loaded in the cell, the voltage between the electrodes was increased in increments of 0.25 V every 5 s, and the current was measured 2 s after every step change (to avoid current spikes). All of the emulsions for which we have reported cef showed no water resolved after a 24 h period. The presence of resolved water would have indicated an emulsion containing large, unstable droplets. All of the emulsions tested were relatively stable and had droplet diameters in the range of 0.5−20 μm. All of the crude oil systems appeared to have droplet size ranges that were close enough to ensure valid comparisons from sample to sample. Model oil emulsion studies were conducted in the same manner except all steps were performed at room temperature.

ICP Metal Content Analysis. The metal content (V, Ni, and Fe) of the asphaltene samples were determined by means of an Optima 2000 DV, Scanning CCD, ICP optical emission spectrometer, Perkin-Elmer Instruments, Norwalk, CT.

Results and Discussion

Water-in-Oil Emulsion Stability. As typical examples of asphaltene-stabilized emulsions, water-in-crude oil and water-in-model oil emulsions were studied, both known to be strongly stabilized by asphaltenes. Emulsion stability was characterized by critical electric fields, i.e., the electric field required to sufficiently
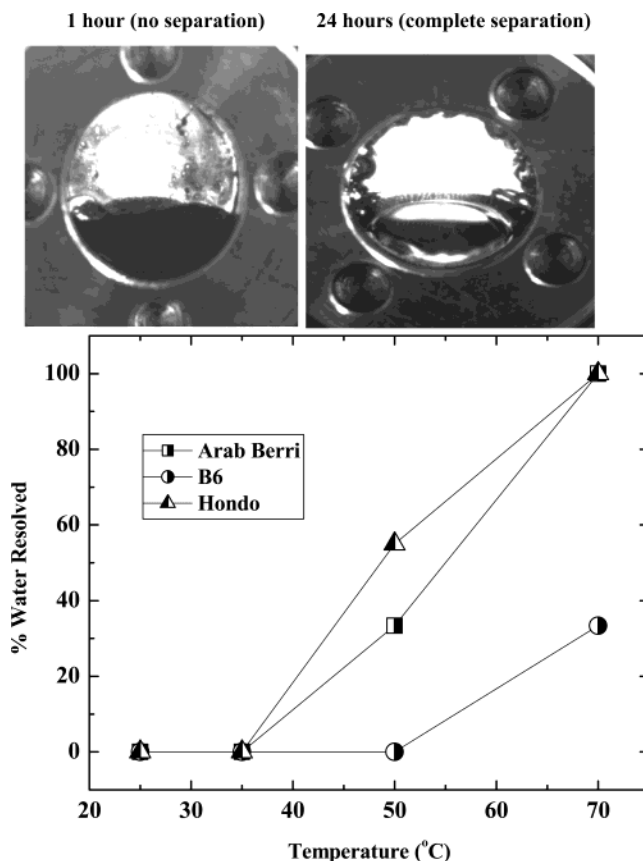

Figure 2. Dependence of % water resolved on temperature with crude oil emulsions containing 60 vol % water and contacted with CO_2 at 1500 psi and 24 h contact time.

polarize emulsified micron-sized water droplets to induce coalescence of the emulsion.[28−32] The crude oil emulsions studied included emulsions of 30 and 60% water (v/v) dispersed in Arab Berri, Hondo, and B6 crudes. Hondo and B6 crudes are asphaltenic heavy crudes, while Arab Berri is a light, low-asphaltene crude. The resin to asphaltene (R/A) ratio in B6 is significantly lower than Hondo, and thus the surface activity and aggregate size of the asphaltenes in B6 are greater, as is the viscosity. The 30% w/o emulsions for AB, B6, and HO had critical electric fields of 0.26, 1.71, and 2.88 kV/cm, respectively, a significant range of emulsion stabilities.[33−35] We also studied water-in-model oils in which asphaltenes were dissolved and in which the aromaticity of the oil was systematically varied from pure toluene to mixtures of heptane and toluene.[12]

Destabilization of Water-in-Crude Oil Emulsions. Emulsions of 60% water-in-crude oil were contacted with compressed CO_2 at various temperatures (25−70 °C), pressures (1000−4500 psia), and contact times. At CO_2 contacting pressures of 1500 psia, and residence times of 24 h, the temperature of the system had a significant effect on demulsification (see Figure 2). Both AB and B6 w/o emulsions showed no water resolution at 30 °C but were completely demulsified at 70 °C after 24 h of contact with CO_2. Photographs of a water-in-B6 crude emulsion after 1 and 24 h of contacting with 1500 psi CO_2 at 70 °C are also shown in Figure 2, clearly illustrating the long time required for demulsification. Clearly, the demulsification rate increases markedly with temperature. The temperature dependence of the demulsification may be due in part to the
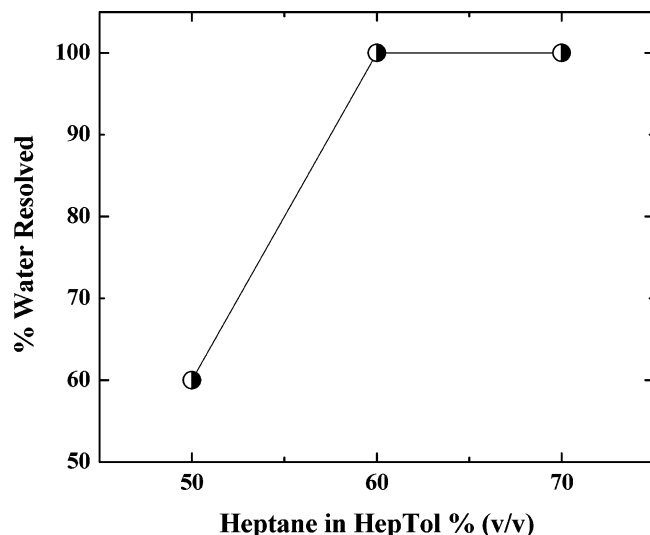
Figure 3. Effect of heptane−toluene solvency on emulsion destabilization with model emulsions containing 60 vol % water in oil contacted with CO_2 at 1500 psi, 50 °C, and 24 h contact time.

decrease in crude oil viscosity with increasing temperature, which decreases the intrinsic stability of the emulsions.

To ensure that the demulsification was exclusively due to the action of CO_2, a number of control experiments were performed using compressed N_2 rather than CO_2. Under conditions at which 100% of the emulsified water was resolved with B6 crude oil, 1500 psia CO_2 at 24 h residence time and 70 °C, no water was observed to resolve with nitrogen as the compressing gas. We also investigated whether the slight acidity of the emulsion's aqueous phase due to dissolution of CO_2 is responsible for the emulsion instability. Acetic acid (0.25 vol/vol % of the water phase of the emulsion at a pH 2.85) was added to the emulsion in the presence of compressed N_2 at the various temperatures and pressures employed when using CO_2. No water separation occurred in the presence of acetic acid, indicating that the low pH of the aqueous phase of the emulsion is not the cause of its instability. It is well-known that crude oil viscosities decrease with increasing amounts of dissolved CO_2 at high pressure,[36] and this lower viscosity can help in the demulsification process.

Destabilization of Water-in-Model Oil Emulsions. To isolate the specific physical mechanism responsible for the observed water-in-crude oil emulsion destabilization by CO_2, we next studied destabilization of water-in-model oil emulsions stabilized by asphaltenes. Three model oils having 50, 60, and 70 vol % heptane in toluene and 3% (w/w) asphaltenes from Hondo crude oil were demulsified with CO_2 at 1500 psi pressure, 24 h residence time, and at 50°C (Figure 3). Increasing the toluene content of Heptol decreases demulsification, apparently due to the reduced ability of CO_2 to precipitate the adsorbed asphaltenes at the interface in case of the well-solvated asphaltenes present in the more aromatic 50:50 Heptol solvent. In the cases of the 60:40 and 70:30 Heptol, it was possible to completely destabilize the emulsion due to the relative ease of asphaltene precipitation from the water/oil interface. When the same experiments were repeated for the same emulsions using liquid CO_2 instead of SC CO_2 (at 25 °C and 1500 psi) and at the same contact time (24 h), no water separation was observed. This may be attributed to the enhanced solubility of SC CO_2 in
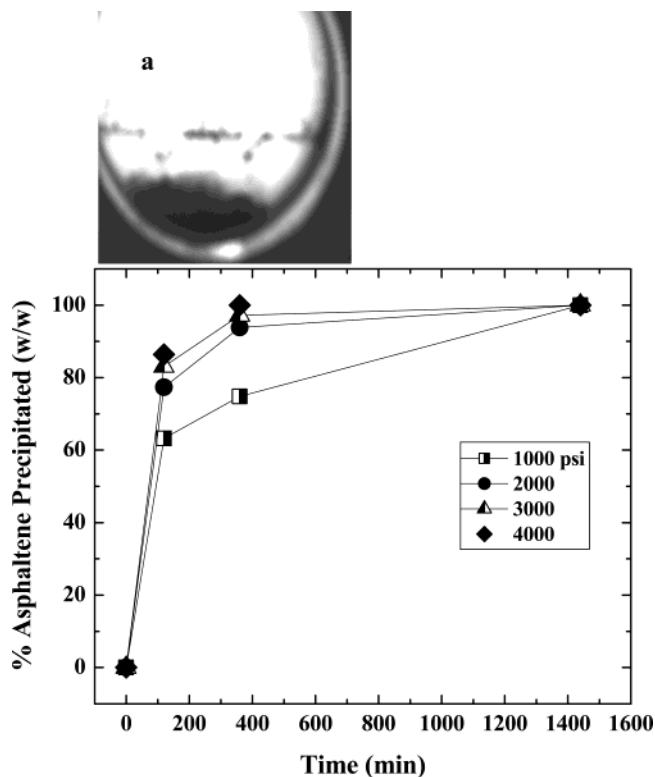

Figure 4. Asphaltene precipitation (w/w) as a function of CO_2 pressure and contact time at 25 °C with solutions of 1% (w/w) B6 asphaltenes dissolved in toluene and contacted with CO_2. (a) Photograph showing complete asphaltene precipitation (clear toluene + dense CO_2 phase) taken after 24 h contact time with CO_2 @ 2000 psi and 25 °C.

Heptol at 50 °C as compared to that of liquid CO_2 at 25 °C. The enhanced solubility and diffusivity of SC CO_2 in Heptol reduce the solvent ability of the oleic phase for asphaltenes, resulting in increased asphaltene precipitation and emulsion destabilization.

Asphaltene Precipitation by CO_2. To determine the potential of an antisolvent effect of CO_2 in destabilizing emulsions by asphaltene precipitation, we have studied the precipitation of asphaltenes dissolved in toluene, a good solvent, upon dissolution of CO_2. Asphaltene precipitation occurred when compressed CO_2 was contacted with a 1 wt % B6 asphaltene in toluene solution at 25 °C and 1000 psi CO_2 pressure (Figure 4). When CO_2 was depressurized, the precipitated asphaltenes redissolved in toluene, and complete asphaltene solubility occurred when all CO_2 was removed from the solvent. This experiment illustrates the antisolvent effect of dense CO_2 toward asphaltenes, and that asphaltenes can be completely precipitated when CO_2 is dissolved in the organic solvent.

From the results above, we infer that CO_2 destabilizes water-in-crude oil emulsions by asphaltene flocculation and precipitation. Asphaltenes adsorb and self-associate at the water/oil interface to form mechanically strong elastic interfacial films.[37]

To destabilize the emulsion, the asphaltene film must be presumably disrupted, leading to film thinning and water coalescence. When compressed CO_2 is employed, it apparently flocculates and precipitates the asphaltenic film, rendering the film less elastic and more brittle. In this physical state, the asphaltenes are more easily displaced from the interface and into the bulk oil phase as the oleic films between water droplets thin and
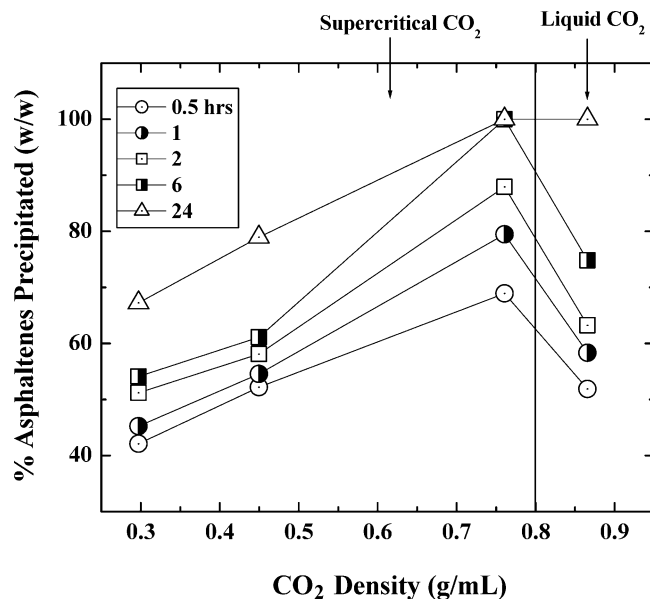
Figure 5. Asphaltene precipitation (w/w) as a function of CO_2 density and at different contact times (temperature range: $25-100$ °C, pressure range: $1000-5000$ psi) with solutions of 1% (w/w) B6 asphaltenes dissolved in toluene and contacted with CO_2.

Figure 6. Asphaltene precipitation with CO_2 as a function of solvent H/C ratio at 25 °C, 1000 psi CO_2 pressure, and 2 h contact time with solutions of 1% (w/w) B6 asphaltenes dissolved in toluene and contacted with CO_2.

the droplets coalesce. In combination with the lower oil viscosity in the presence of high-pressure CO_2, this phenomenon can facilitate transfer of water from one droplet to another to accelerate flocculation.

The rate of precipitation of asphaltenes dissolved in pure toluene by CO_2 was studied as a function of the temperature and pressure of the compressed CO_2. Figure 4 shows the effect of pressure at 25 °C on the kinetics of asphaltene precipitation. Clearly, the majority of CO_2 dissolution and subsequent asphaltene precipitation occurs in the first 100 min. As the density of the CO_2 is increased (at higher pressure or lower temperature, above the critical temperature of 31 °C), the initial rate of precipitation is increased. This is consistent with the rate of dissolution of CO_2 into the oil phase dictating the initial precipitation rate. The equilibrium solubility of CO_2 in toluene is likely increased as the pressure is increased as well, although at all pressures studied here, the asphaltenes were completely precipitated after 24 h. It is clear from the photograph present in Figure 4, which was taken for a 1 wt % B6 asphaltenes in toluene solution contacted for 24 h. with CO_2 @ 2000 psi and 25 °C, that complete asphaltene precipitation occurred leaving a clear toluene solvent behind.

The effect of CO_2 density on the rate of asphaltene precipitation from its solution in toluene is shown in Figure 5. It is clear that the rate of asphaltene precipitation increases with density in the supercritical region, and a decrease in the asphaltene precipitation occurs when CO_2 is in the liquid form. The temperatures used were 25 °C at which CO_2 is in the liquid form (subcritical) and 40, 70, and 100 °C at which CO_2 is in its supercritical form. Supercritical CO_2 is a better solvent for toluene as compared to liquid CO_2 simply because it is more dense and has a higher diffusivity. The enhanced solubility of supercritical CO_2 in toluene will eventually lead to a change in the solubility parameter of the toluene toward asphaltenes leading to its precipitation. Recalling the data obtained for the demulsification of different crude oils by CO_2 at different temperatures (Figure 2), we have seen that the rate of
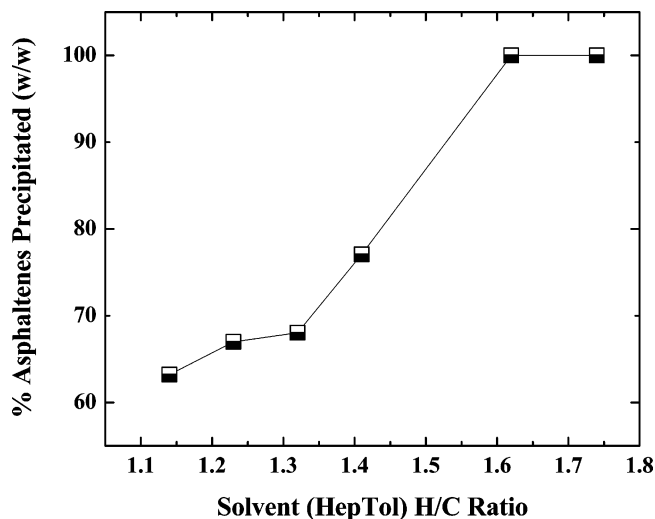
demulsification was found to increase by increasing the temperature, we explained that in terms of decreasing the viscosity of the crude oil; however, for low-viscosity crude oils as Arab Berri, it is not the viscosity of the crude oil that causes its emulsions to be stable, it is the state of asphaltene aggregation at the water/oil interface. It is apparent that increasing the temperature causes an enhanced solubility of CO_2 in the crude oil and hence making it less favorable solvent for asphaltenes and hence causing a faster rate of asphaltene precipitation.

Effect of the Solvent Aromaticity (H/C) Ratio. As crude oil chemistries and H/C ratios vary, the state of asphaltene aggregation and their ability to adsorb at the oil/water interface will vary as well. Asphaltenes were dissolved in solvent mixtures composed of different heptane−toluene ratios, and the solutions were subjected to compressed CO_2 at different temperatures and pressures. The results of these experiments are shown in Figure 6. This plot shows the wt % of precipitated asphaltenes as a function of the solvent H/C ratio at constant temperature (25 °C), CO_2 pressure (1000 psi), and contact time (120 min). As expected, the greater the H/C ratio (more aliphatic character) of the solvent, the larger the amount of asphaltene precipitation by CO_2.

The tendency of asphaltenes to aggregate in solution is pronounced and depends strongly on solvent strength. While isolated asphaltene "monomers" have an average molecular mass of the order of 1000 g/mol,[38] several methods including VPO, SEC, and scattering techniques (SAXS, SANS) show that they associate spontaneously in solution, resulting in aggregates of 10 000 g/mol or higher (VPO) with physical dimensions from 10 to 100 nm (SAXS, SANS)[39,40]

In poor solvents conditions asphaltenes aggregate into clusters and flocs that are unstable and precipitate, according to the scheme shown below.[41]

asphaltene molecules → micelles →
        micelle clusters/flocs → precipitates

Effect of Resins to Asphaltene Ratio. Resins are the most surface-active fraction of crude oils and are believed to adsorb onto the asphaltenic aggregates and
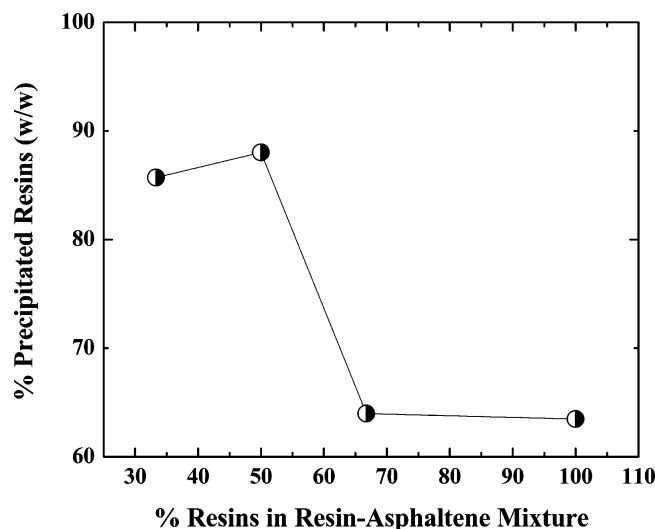
Figure 7. Resin precipitation as a function of the percentage of resins in a resin–asphaltene mixture at 25 °C, 1000 psi CO_2 pressure, 2 h contact time, and 50:50 heptane/toluene solvent composition.

Figure 8. Influence of adding water on the kinetics of asphaltene precipitation at 25 °C and 1000 psi CO_2 pressure.

act as solvating agents.[42–44] Resins play an important role in stabilizing asphaltenes in crude oil.[45,46] They differ from asphaltenes in that they have a lower molecular weight and are soluble in both heptane and toluene. VPO and scattering studies [47,48] on resin fractions show that they self-associate in organic solvents. Resin and asphaltene fractions are probably best viewed as two "adjacent" portions of a single broad compositional continuum that contains the more polar, aromatic, and higher molecular weight components of petroleum. Resins compared to asphaltenes are less aromatic (have higher H/C ratio) and have lower molecular weights[49] than asphaltenes. The resin content of crude oils varies markedly from one crude oil to another, ranging from 3 to 40 wt %. A hypothesized solvating structure of asphaltenes was proposed by Pfeiffer and Saal,[50] in which asphaltenes form a polynuclear aromatic dense core that is solvated strongly by resins or maltenes.

The effect of B6 resins on the amount of B6 asphaltene precipitation upon contacting with dense CO_2 was investigated. Figure 7 shows the amount of precipitated resins as a function of the R/A ratio. In these experiments, solutions containing a fixed resin concentration (1 wt/vol %) and variable concentrations of asphaltenes (2, 1, and 0.5 wt/vol %, respectively) were dissolved in a solvent composed of 50 vol % toluene and 50 vol % *n*-heptane and pressurized with 1000 psi CO_2 @ 25 °C and contact time 24 h. At these conditions, 100% of the asphaltenes had already been precipitated with CO_2, and it was our aim to determine the amount of resin precipitated at different R/A ratios. It is clear that the highest rate of resin precipitation occurred at an R/A value equals one. This means that there may be a mutual coprecipitation of the asphaltenes and resins by CO_2 that originates as a consequence of the mutual interaction between asphaltenes and resins. When the ratio of resins to asphaltenes increases, a pronounced decrease in the amount of precipitated resins occur. This may be attributed to the fact that the decreased number of asphaltenes molecules resulted in less coprecipitation of resins

Effect of Water on Asphaltene Precipitation. The systems of greatest interest are those in which the crude
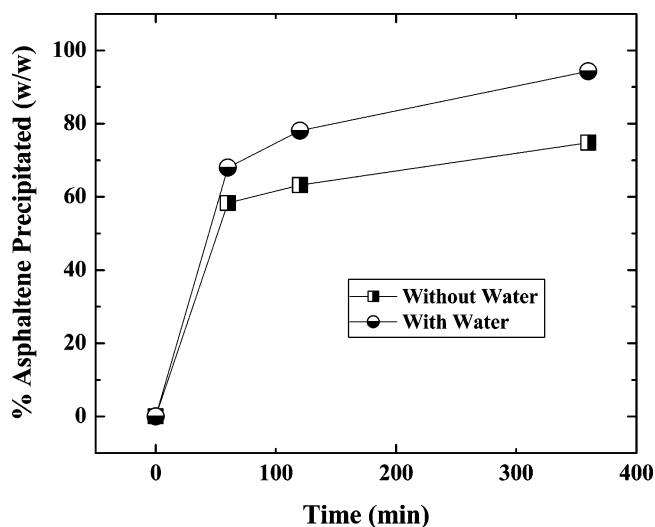
oil contains water droplets, so it is of interest to understand the effect of oil–water interfaces on asphaltene precipitation by CO_2. Figure 8 shows that the amount of asphaltene precipitation in the presence of water is higher than in the absence of water. This is attributed to the fact that asphaltenes adsorbed at the water/oil interface are in higher degree of association and higher concentration than the asphaltenes present in the bulk phase. Asphaltene aggregates are formed in the bulk phase whose size depends on the solvent. At the water/oil interface primary aggregates adsorb and stack via interactions mediated by aromatic π-bonds and hydrogen bonds to form discotic lamellar structures which stabilize the emulsions.[43]

Characterization of the Precipitated and CO_2– Soluble Asphaltene Fractions. Asphaltenes dissolved in toluene were fractionated with CO_2 addition at 35 °C and at 2000 psi pressure for 120 min contact time. Two fractions were obtained, the CO_2-insoluble fraction and the CO_2-soluble fraction, and they were analyzed for their molecular weight, elemental analysis, C, H, N, O, and S, and metal content, Fe, Ni, and V. The results are tabulated in Table 2.

Several conclusions can be drawn from the data present in this table. As might be expected, the insoluble fraction (IF) has a higher molecular weight than the average for all the asphaltenes and the soluble fraction (SF) has a lower molecular weight. The IF also has a higher content of oxygen, sulfur, and nitrogen than the SF and is therefore more polar and more likely to form aggregates in the bulk solution.

Kassim et al.[51] described a method of crude oil fractionation by CO_2 near its critical point. They found that the number average molecular weight of the fractions of the extracted hydrocarbons from crude oil differed markedly from the original crude oil. A crude oil of 414 g mol^{-1} molecular mass yielded three fractions and a residue obtained from the crude oil at three different CO_2 pressures: 1430, 1638, and 1712 psi. The crude oil fractions obtained had molecular masses of 210, 254, and 282 g mol^{-1}, respectively, and 515 g mol^{-1} for the residue. It was found that the fraction obtained at the highest CO_2 pressure (1712 psi) had the lowest asphaltene content. This is consistent with the results obtained in this work showing that the CO_2-insoluble fraction had the highest molecular weight and that

Table 2. Analysis of the Different Asphaltene Fractions

asphaltene fraction	aliph/arom proton ratio	H/C ratio	mol wt.	C (w/w %)	H (w/w %)	O (w/w %)	N (w/w %)	S (w/w %)	V (ppm)	Ni (ppm)	Fe (ppm)
whole	14.1:1	1.24	5590	79.54	8.20	2.09	1.72	8.12	1018	373	168
CO_2−insoluble (AIF)	12.4:1	1.23	5968	79.66	8.18	2.24	1.97	8.28	1381	291	319
CO_2−soluble (ASF)	18.7:1	1.36	1465	80.62	9.16	1.72	0.89	7.80	755	438	45

higher CO_2 pressures result in larger amounts of asphaltene precipitation.

The ^{1}H NMR results in Table 2 indicate that the aliphatic/aromatic protons ratio is highest for the SF and lowest for the IF indicating that the IF is most aromatic, while the ASF is the most aliphatic. These results are confirmed by the elemental analysis that shows that the IF has the lowest H/C ratio (most aromatic), while the SF has the highest H/C ratio. Apparently, both the aromaticies and polarities of the different fractions control their solubility in CO_2. In some cases, the solvency power of CO_2 is comparable to that of *n*-hexane.[52] It is thus expected that as the aromaticity of a certain fraction increases its solubility in CO_2 decreases.

The metal analysis shows that the IF contains the highest Fe, Ni, and V content. These metals are typically present in the asphaltene molecule in organometallic cyclic structures called porphyrins, pyrollic rings interconnected by methylene bridges. In light of the higher aromaticity of the IF and its higher nitrogen content, it is likely to have the highest porphyrin content; consequently, it is not surprising that the IF has the highest metal content due to the potential for chelation within the porphyrin structure. Our findings confirm those reported by a number of authors[53−55] who studied the use of dense CO_2 in crude oil deasphalting and demetalling. They found that the use of dense CO_2 in combination with *n*-heptane and *n*-pentane substantially decreased the metal content of heavy crudes as compared to the crude oils treated with *n*-heptane or *n*-pentane in absence of CO_2.

The role of porphyrin-containing molecules in stabilizing w/o emulsions was studied by Denekas et al.[56] and Dodd et al.[57] They concluded that resins, waxes, and porphyrin-containing compounds were all present in the film-forming fraction. The importance of porphyrin-containing materials from asphaltenes in strengthening interfacial films at oil−water interfaces has been independently confirmed by Mansurov et al.[58] They found that the shear strength of the asphaltenic films formed in mineral oil−xylene−water−0.1% asphaltene mixtures, as measured by a torsion pendulum rheometer, was reduced by as much as 50% upon removal of the porphyrins by acetone extraction. Potentially, other materials were extracted in their experiments. However, their results do support the notion that porphyrin functional groups play a role in enhancing the strength of asphaltene interfacial films. Consequently, as CO_2 is demonstrated to precipitate preferentially the porphyrin-containing portion of asphaltenes, the efficacy of CO_2 in destabilizing the asphaltenic interfacial film can be safely inferred.

Demulsification Kinetics of Water-in-Model Oil Emulsions. The kinetics of water separation (demulsification) of water-in-model oil emulsions at 2000 psi CO_2 pressure and at different temperatures (25−100 °C) are shown in Figure 9. Increasing the temperature from 25 to 35 °C (crossing the critical temperature of CO_2 at 31 °C) results in a substantial increase in the amount of separated water (from 10 to 25%) after 120 min. A
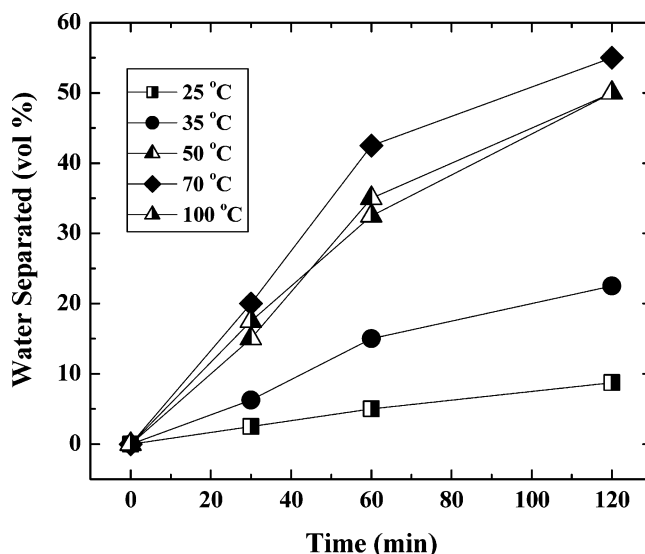

Figure 9. Dependence of amount of water separated (v/v %) of water-in-model oil emulsions at different temperatures and at 2000 psi CO_2 pressure.
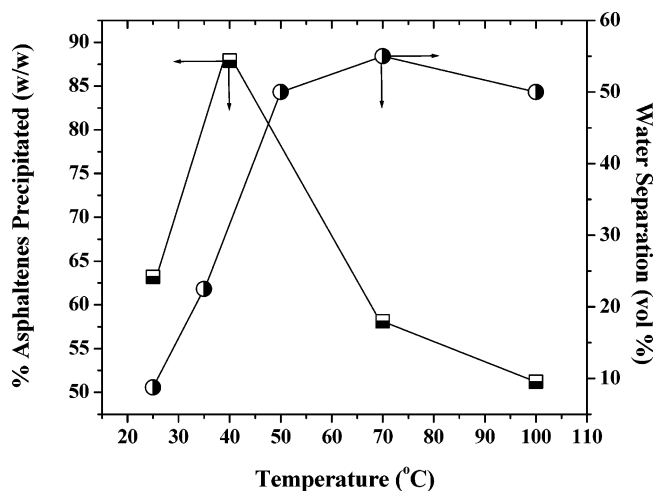

Figure 10. Dependence of water separation and asphaltene precipitation on temperature at 2000 psi CO_2 pressure and 2 h contact time.

further increase in temperature from 35 to 70 °C increases the amount of water separated to 50%. Subsequent increases to 100 °C had little effect on the amount or rate of water separation. Figure 10 shows both the amount of separated water and the amount of precipitated asphaltenes as a function of temperature after a 120-min contact time with CO_2 at 2000 psi. The amounts of precipitated asphaltenes and separated water increase initially with temperature when crossing from liquid to supercritical CO_2. However, further increases in temperature decrease the amount of precipitated asphaltenes and increase the amount of separated water. The decrease in asphaltene precipitation with increasing temperature is likely due to the decreased density of CO_2 at these higher temperatures. The results in Table 3 show that the amount of water separated from the emulsions increased when the CO_2
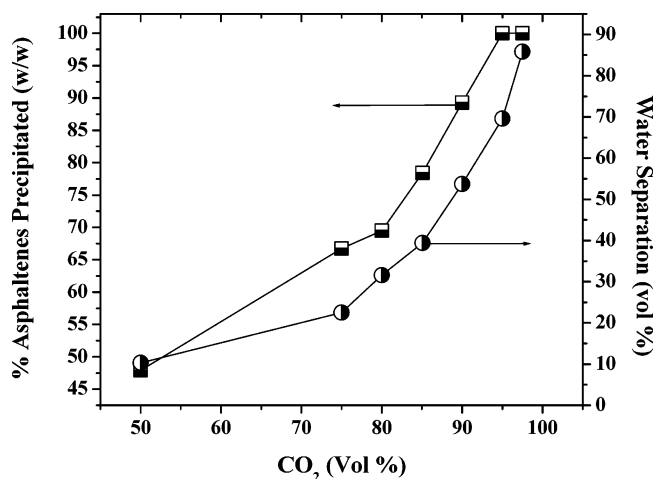
Figure 11. Asphaltene precipitation and water separation as a function of CO_2 volume % at 35 °C, 2000 psi CO_2 pressure, and 2 h contact time.

Table 3. Increase in Water Separated with CO_2 Pressure

	% water separated after 2 h contact time	
temp (°C)	at 2000 psi	at 3000 psi
25	9	25
35	23	33
50	50	65
70	55	75
100	50	67

pressure was raised from 2000 to 3000 psi at different temperatures after 2 h contact time. This is due to the increase in CO_2 density with pressure, which causes more asphaltene precipitation and faster demulsification kinetics due to reduced asphaltene solubility. The increased demulsification rate with temperature at a fixed pressure may be due to the lowering of the viscosity of the oil phase, and the increase in the density difference between the water and oil phase.[59] These factors also tend to enhance collisions between water emulsion droplets and can result in enhanced water separation.

Effect of Phase Volume Ratio on Demulsification. A series of experiments were undertaken to assess the effect of CO_2/emulsion phase volume ratio on the rate of demulsification of water-in-model oil emulsions. The model oil was composed of 45 vol % heptane and 55 vol % toluene containing 1 wt/vol % B6 asphaltenes. The CO_2/emulsion phase volume ratio was varied, while CO_2 pressure, contact time, and the emulsion constituents were kept constant. The results of a series of experiments determining the effect of CO_2 vol % on % water separation at 35 °C are shown in Figure 11. Increasing the CO_2 volume % from 50 to 97.5% increases the % water separated from 10.3 to 85.8%. The amount of precipitated asphaltenes from model oil increases with increasing the CO_2 vol % in a very similar fashion. It is clear that the amount of separated water is directly related on the amount of precipitated asphaltenes at a particular pressure, temperature, CO_2 vol %, and contact time. This explains why injecting the emulsion into CO_2 causes much faster water separation, and that the water separation is closely related to the rate of asphaltene precipitation from the water/oil interface. It is important to recognize that only a portion of the asphaltene molecules adsorb and consolidate at the water/oil interface. The amount of adsorbed asphaltenes depends on the total water−oil interfacial area, which

in turn depends on the water content and water mean droplet size. It is thus not surprising that partial precipitation of the asphaltene molecules present at the water/oil interface is sufficient to affect emulsion destabilization. This is particularly important because the solubility of dense CO_2 in the heptane and toluene mixture that forms the model oil is much higher than the solubility of dense CO_2 in crude oils formed of a much more complex mixture of hydrocarbons with higher molecular weights than those of heptane and toluene. Consequently, the amount of precipitated asphaltenes from crude oil systems is expected to be lower than the amount of precipitated asphaltenes from model oils. Srivastava et al.[60] in their study of asphaltene flocculation during miscible CO_2 flooding, showed that asphaltenes begin to flocculate at a CO_2 concentration of about 42 mol %. After this onset, it has been found that there is a linear increase in asphaltene flocculation with increasing CO_2 pressure.[61,62] Because of the importance of phase volume ratio and high pressure on asphaltene precipitation, it is likely that an injection mode might be preferred to obtain rapid demulsification of water-in-crude oil emulsions in the field.

Enhanced Demulsification Kinetics. The demulsification experiments discussed up to now were all done in batch systems at fixed temperatures and pressures and at fixed contact times. In this type of operation, demulsification rates can be quite slow due to the time required for mass transfer of the CO_2 into the oil and aqueous phase as well as the time required for asphaltene aggregates to precipitate out of solution and water droplets to coalesce and rise to the surface.

To demonstrate the potential utility of the use of dense CO_2 for more rapid demulsification of water-in-crude oil emulsions, a flow system was designed in which the emulsion was extruded or injected into a vessel containing CO_2 at high pressure. The experimental apparatus used for executing these experiments is described in Experimental Section and depicted in Figure 1. An emulsion composed of 30% water-in-B6 crude oil was placed into a high-pressure reactor, pressurized with CO_2 at 2000 psi, and the temperature was maintained at 70 °C. The first view cell was pressurized with CO_2 at 1000 psi, and the temperature was maintained at 35 °C. The emulsion was injected into the first view cell at a flow rate of 1 mL/min (10 mL of the emulsion was delivered in approximately 10 min). Partial water coalescence occurred due to the initial pressurization of the emulsion with CO_2, which led to an increase in the average size of the dispersed water droplets. During the delivery process, water droplets were seen separating from the oil and residing at the bottom of the first view cell (Figure 12a), then they started to form a separate water phase (Figure 12b). At the end of the 10-min period, the separated water phase was forced under CO_2 pressure from the bottom of the first view cell to the second view cell until all of the water was delivered. CO_2 was depressurized to separate it from the water phase. At the end of the process, the second view cell was opened and the amount of water was quantified. Complete water separation of the water occurred in 10 min instead of 24 h as we obtained from the previous regime. A control experiment was performed in which the emulsion was pressurized with nitrogen gas and injected under pressure into a pressure vessel pressurized with nitrogen. No water separation occurred when nitrogen was used
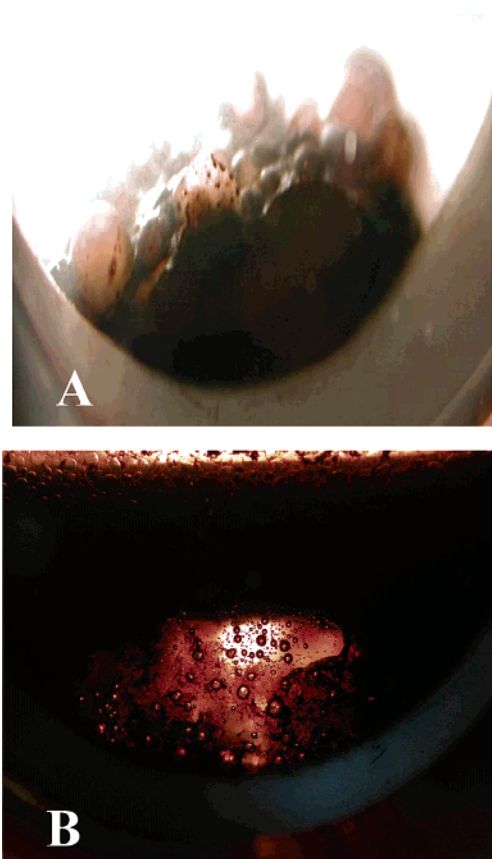
Figure 12. (A) Photograph showing the peeled asphaltene layer from the surface of the separated water droplets during injection of the crude oil emulsion (30% water-in-B6 crude oil) into dense CO_2. (B) Photograph showing the water phase separated from the oil phase after the completion of the process of injection of the B6 crude oil emulsion into dense CO_2, approximately five minutes after injection commenced.

instead of CO_2, indicating that the CO_2 antisolvent effect toward asphaltenes is the main driving force for demulsification. This enhanced kinetics of demulsification results in part from subjecting the emulsion to an excess of CO_2 as it is injected into the pressurized chamber. The phase volume ratio between CO_2 and the oil in the flow process was kept very high at all times. Furthermore, the emulsion was contacted with CO_2 twice, initially in the high-pressure reactor, and for the second time in the first view cell.

Figure 12a is a photograph obtained immediately upon injection of the emulsion into dense CO_2 under pressure. In this photograph, the asphaltene film adsorbed at the water droplets (appears brownish yellow in color) starts to precipitate (peel) upon contact with the dense CO_2 antisolvent. The peeling of the asphaltenic film, led to water droplets' coalescence, and emulsion breakdown.

Conclusions

CO_2 was used successfully to break water-in-crude oil emulsions and resolve bulk water. The new process was found to be applicable to crude oils having different chemistries, asphaltene content, and viscosities. The mechanism by which CO_2 destabilizes the emulsion was found to involve the precipitation of asphaltenes due to the antisolvent effect of CO_2. The amount and rate of asphaltene precipitation were measured and found to increase with pressure, temperature, and the presence

of water. Asphaltenes were fractionated with CO_2 into a CO_2-soluble fraction (SF) and insoluble fraction (IF). Analysis indicated the insoluble fraction is more aromatic, and has a higher molecular weight, and a higher content of the elements oxygen, sulfur, nitrogen, vanadium, nickel, and iron than the whole asphaltene or soluble fraction. CO_2 precipitates the most polar and metal-containing portion of asphaltenes that is believed to be more surface active and a stronger film former than the soluble fraction which is less polar and has lower surface activity and film forming capacity. The rate of the demulsification process was greatly enhanced when the emulsion was injected under pressure into compressed CO_2. This enhanced demulsification kinetics is attributed to the increased dense CO_2-emulsion phase volume ratio, which causes more asphaltene precipitation in much shorter time. The new method shows promise as an environmentally friendly substitute to chemical demulsifiers currently utilized for breaking water-in-crude oil emulsions.

Acknowledgment

Literature Cited

(1) McLean, J. D.; Spiecker, P. M.; Sullivan, A. P.; Kilpatrick, P. K. *The Role of Petroleum Asphaltenes in the Stabilization of Water-in-Oil Emulsions. Chapter XII in Structures and Dynamics of Asphaltenes*; Mullins, O. C., Sheu, E. Y., Eds.; Plenum Press: New York, 1998; pp 377−422.

(2) Schramm, L. L., Ed. *Emulsions: Fundamentals and Applications in the Petroleum Industry*; In *Advances in Chemistry Series*; American Chemical Society: Washington, DC, 1992.

(3) Yarranton, H. W.; Hussein, H.; Masliyah, J. H. Water-in-Hydrocarbon Emulsions Stabilized by Asphaltenes at Low Concentrations. *J. Colloid Interface Sci.* **2000**, *228*(1), 52−63.

(4) Taylor, S. E. Resolving Crude Oil Emulsions. *Chem. Ind.* **1992**, *20*, 770−773.

(5) Kilpatrick, P. K.; Spiecker, P. M. *Asphaltene Emulsions, in Encyclopedic Handbook of Emulsion Technology*; Sjoblom, J., Ed.; Marcel Dekker: NY, 2000; pp 707−730.

(6) Sullivan, A. P.; Zaki, N. N.; Kilpatrick, P. K. The Stability of Water-in-Crude and Model Oil Emulsions. *Colloids Surf. A*, to be submitted.

(7) Khristov, K.; Taylor, S. D.; Czarnecki, J.; Masliyah, J. Thin Liquid Film Technique - Application to Water−Oil-Water Bitumen Emulsion Films. *Colloid Surf. A* **2000**, *174*, 183−196.

(8) Sjöblom, J.; Urdahl, O.; Hoiland; H.; Christy; A. A.; Johansen; E. J. Water-in-Crude Oil Emulsions. Formation, Characterization, and destabilization. *Prog. Colloid Polym. Sci.* **1990**, *82*, 131−139.

(9) Mardanenko, V. P.; Benkovskii, V. G. Separation and investigation of natural emulsifiers for water and crude oils. *Khim. Tekhnol. Topl. Masel.* **1965**, *10*(7), 41−5.

(10) Petrov, A. A.; Pozdnyzhev, G. N. *Chem. Technol. Fuels Oils* **1969** (March), 11−14.

(11) McLean, J. D.; Kilpatrick, P. K. Effects of Asphaltene Solvency on Stability of Water-in-Crude-Oil Emulsions. *J. Colloid Interface Sci.* **1997**, *189*, 242−253.

(12) McLean, J. D.; Kilpatrick, P. K. Effects of Asphaltene Aggregation in Model Heptane-Toluene Mixtures on Stability of Water-in-Oil Emulsions. *J. Colloid Interface Sci.* **1997**, *196*, 23−24.

(13) Singh, S.; McLean, J. D.; Kilpatrick, P. K. Fused Ring Aromatic Solvency in Destabilizing Water-in-Asphaltene-Heptane-Toluene Emulsions. *J. Dispersion Sci. Technol.* **1999**, *20*, 279–293.

(14) Zaki, N. N.; Al-Sabagh, A. M. De-emulsifiers for Water-in-Crude Oil Emulsions, The Efficiency of Polyalkyl phenols Polyalkylenepolyamines formaldehyde ethoxylates as Demulsifiers for Water-in-Crude Oil Emulsions. *Tensides Surfactants Deterg.* **1997**, *34*(1), 12–17.

(15) Zaki, N. N.; Maysour, N. E.; Abdel-Azim, A. A. Polyoxyalkylenated Amines For Breaking Of Water-In-Oil Emulsions. 1. Effect of Structural Variations on the Demulsification Efficiency. *Polym. Adv. Technol.* **1998**, *9*(2), 159–166.

(16) Zaki, N. N.; Abdel-Raouf, M. E.; Abdel-Azim, A. A. Polyoxyethylenated Bisphenol-A for Breaking Water-in-Oil Emulsions. *Polym. Adv. Technol.* **1996**, *7*, 805–808.

(17) Ohsol, E. O.; Pinkerton, J. W.; Gillespie, T. E.; Laity, T. H. Process for Upgrading Heavy Crude Oil Production. U.S. Patent 5,948,242, 1999.

(18) Hart, P. R. Method of Breaking Reverse Emulsions in a Crude Oil Desalting System. U.S. Patent 5,607,574, 1997.

(19) Mitchell, K. E. Crude Oil Desalting Process. U.S. Patent 5,746,908, 1998.

(20) Little, C. T. Removal of Petroleum Hydrocarbons from Oil-Field Brines with Carbon Dioxide. Ph.D. Dissertation, The University of Texas at Austin, 1990.

(21) Burke, N. C.; Curtice, S.; Little, C. T.; Seibert, A. F. Removal of Petroleum Hydrocarbons from Oil-Field Brines with Carbon Dioxide. *SPE J.* **1991**, SPE paper 21046, 457–465.

(22) Auflem, I. H.; Kallevik. H.; Westvik, A.; Sjoblom, J. Influence of pressure and solvency on the separation of water-in-crude oil emulsions from the North Sea. *J. Pet. Sci. Eng.* **2001**, *31*, 1–12.

(23) Kallevik, H.; Sjoblom, J.; Westvik, A.; Auflem, I. H. Process for Separation of Water and Oil in a Separator by Breaking Water-in-Oil Emulsions. P 4202-1, PCT-application, 23 February 2002.

(24) Auflem, I. H.; Westvik, A.; Sjoblom, J. Destabilization of water-in-oil emulsions based on recombined oil samples at various pressures. *J. Dispersion Sci. Technol.*, submitted.

(25) Wilson, R. E.; Keith, P. C.; Haylett, R. E. Liquid propane-use in dewaxing, deasphalting, and refining heavy oils. *Ind. Eng. Chem.* **1936**, *28*, 1065–1078.

(26) Gearhart, J. A.; Garwin, L. ROSE process improves resid feed. *Hydrocarbon Process.* **1976**, *55*, 125–128.

(27) Urdahl, O.; Williams, T. J.; Bailey, A. G.; Thew, M. T. Electrostatic Destabilization of Water-in-Oil Emulsions Under Conditions of Turbulent Flow. *Trans. Inst. Chem. Eng.* **1996**, *74*, 158–165.

(28) Bailes, P. J.; Larkai, S. K. L. Liquid-Phase Separation in Pulsed D.C. Fields. *Trans. Inst. Chem. Eng.* **1982**, *60*, 115–121.

(29) Chen, T. Y.; Mohammed, R. A.; Bailey, A. I.; Luckham, P. F.; Taylor, S. E. Dewatering of Crude Oil Emulsions 4. Emulsion Resolution by the Application of an Electric Field. *Colloids Surf. A.* **1994**, *83*, 273–284.

(30) Førdedal, H.; Schildberg, Y.; Sjöblom, J.; Voile, J.-L. Crude Oil Emulsions in High Electric Fields as Studied by Dielectric Spectroscopy. Influence of Interaction Between Commercial and Indigenous Surfactants. *Colloids Surf. A* **1996**, *106*, 33–47.

(31) Skodvin, T.; Sjöblom, J. Dielectric Spectroscopy on W/O Emulsions Under Influence of Shear Forces. *Colloid Polym. Sci.* **1996**, *274*, 754–762.

(32) Wang, L.; Yan, Z. The Optimum Frequency in Electrically Enhanced Coalescence of W/O Type Emulsions. *J. Dispersion Sci. Technol.* **1994**, *15*, 35–58.

(33) Førdedal, H.; Nodland, E.; Sjöblom, J.; Kvalheim, O. M. A Muitivariate Analysis of W/O Emulsions in High External Electric Fields as Studied by Means of Dielectric Time Domain Spectroscopy. *J. Colloid Interface Sci.* **1995**, *173*, 396–405.

(34) Sjöblom, J.; Fordedal, H.; Jakobsen, T.; Skodvin, T. *Dielectric Spectroscopic Characterization of Emulsions*; Birdi, K. S., Ed.; CRC Press: Boca Raton, 1997; pp 217–237.

(35) Skodvin, T.; Sjöblom, J.; Saeten, J. O.; Urdahi, O.; Gestblom, B. Water-in-Crude Oil Emulsions from the Norwegian

Continental Shelf IX. A Dielectric Spectroscopic Characterization of Authentic as Well as Model Systems. *J. Colloid Interface Sci.* **1994**, *166*, 43–50.

(36) Sayegh, S. G. Phase Behavior Properties of CO$_2$/Heavy Oil Mixtures for EOR Applications. *SPE J.* **1990**, SPE paper 20037, 227–236.

(37) Li, M.; Xu, M.; Ma, Y.; Wu, Z.; Christy, A. A. Interfacial Film Properties of Asphaltenes and Resins. *Fuel* **2002**, *81*, 1847–1853.

(38) Al-Jarrah, M. M. F.; Al-Dujaili, A. H. Characterization of Some Iraqi Asphalts II. New findings on the Physical Nature of Asphaltene. *Fuel Sci. Technol. Int.* **1989**, *7*, 69–88.

(39) Xu, Y.; Koga, Y.; Strausz, O. P. Characterization of Athabasca Asphaltenes by Small-Angle X-ray Scattering. *Fuel* **1995**, *74*, 960–964.

(40) Tanaka, R.; Hunt, J. E.; Winans, R. E.; Thiyagarajan, P.; Sato, S.; Takanohashi, T. Aggregates Structure Analysis of Petroleum Asphaltenes with Small-Angle Neutron Scattering. *Energy Fuels* **2003**, *17*, 127–134.

(41) Overfield, R. E.; Sheu, E. Y.; Sinha, S. K.; Liang, K. S. SANS study of asphaltene aggregation. *Fuel Sci. Technol. Int.* **1989**, *7*(5–6), 611–24.

(42) Andersen, S. I.; Speight, J. G. Petroleum Resins: Separation, Character, and Role in Petroleum. *Petrol. Sci. Technol.* **2001**, *19*(1–2), 1–34.

(43) Kawanaka, S.; Leontaritis, K. J.; Park, S. J.; Mansoori, G. A. *Thermodynamic and Colloidal Models of Asphaltene Flocculation*; Borchardt, J. K., Yen, T. F., Ed.; American Chemical Society: Washington, DC, 1989; pp 443–458.

(44) Lian, H. J.; Lin, J. R.; Yen, T. F. Peptization Studies of Asphaltene and Solubility Parameter Spectra. *Fuel* **1994**, *73*, 423–428.

(45) Sheu, E. Y.; De Tar, M. M. Storm, D. A.; DeCanio, S. J. Aggregation and Kinetics of Asphaltenes in Organic Solvent. *Fuel* **1992**, *71*(11), 1277–1281.

(46) Nordli, K. G.; Sjoblom, J.; Kizling, J.; Stenius, P. Water-in-Crude Oil Emulsions from the Norwegian Continental Shelf 4. Monolayer Properties of the Interfacially Active Crude Oil Fraction. *Colloids Surf.* **1991**, *57*, 83–98.

(47) Dickie, J. P.; Yen, T. F. Macrostructures of the Asphaltic Fractions by Various Instrumental Methods. *Anal. Chem.* **1967**, *39*(14), 1847–1852.

(48) Papirer, E.; Bourgeois, C.; Siffert, B.; Balard, H. Chemical Nature and Water/Oil Emulsifying Properties of Asphaltenes. *Fuel* **1982**, *61*(8), 732–734.

(49) Speight, J. G. *The Chemistry and Technology of Petroleum*, 2nd ed.; Marcel Dekker: New York, 1991; p 149.

(50) Pfeiffer, J. Ph.; Saal, R. N. Asphaltic bitumen as colloid system. *J. Phys. Chem.* **1940**, *44*, 139–149.

(51) Kassim, O. M.; Al-Jarah, M. M. F.; Apikian, R. L.; Al-Asaf, S. A. Near Critical Carbon Dioxide Fractionation of Crude Oil 1. Dependence of the Molecular Weight of the Fractions on the Pressure Used. *Fuel Sci. Technol. Int.* **1989**, *7*(2), 207–15.

(52) Taylor, L. T. *Supercritical Fluid Extraction*; John Willey & Sons: New York, 1996; p 14.

(53) Obah, B.; Neumann, H. Deasphalting of Crude Oil Distillation Residues with CO$_2$. *Erdoel Kohle, Erdgas, Petrochem.* **1987**, *40*(11), 486–489.

(54) Eckermann, B.; Vogelpohl, A. Deasphaltization and Demetalling of Heavy Crude Oils and Distillation Residues with C0$_2$. *Chem. Eng. Technol.* **1990**, *13*, 258–264.

(55) Hocker, J.; Vogelpohl, A. New Methods for Deasphalting Residues of Petroleum Distillation. *Chem. Eng. Technol.* **1987**, *10*, 125–131.

(56) Denekas, M. O.; Carlson, F. T.; Moore, J. W.; Dodd, C. G. Materials Adsorbed at Crude Petroleum-Water Interfaces. *Ind. Eng. Chem.* **1951**, *43*, 1165–1168.

(57) Dodd, C. G.; Moore, J. W.; Denekas, M. O. Metalliferous Substances Adsorbed at Crude Petroleum-Water Interfaces. *Ind. Eng. Chem.* **1952**, *44*(11), 2585–2590.

(58) Mansurov, I. R.; Il'yasova, E. Z.; Vygovskoi, V. P. Shear Strength of Interfacial Films of Asphaltenes. *Chem. Technol. Fuels Oils* **1987**, *23*(1−2), 96−98.

(59) Lissant, K. J. *Demulsification Industrial Applications*; Marcel Dekker: NY, 1983; p 123.

(60) Srivastava, R. K.; Huang, S. S.; Dyer, S. B. Quantification of Asphaltene Flocculation During Miscible CO_2 Flooding in the Weyburn Reservoir. *J. Can. Petrol. Technol.* **1995**, *34*(8), 31−42.

(61) Monger, T. G.; Trujillo, D. E. Organic deposition during carbon dioxide and rich-gas flooding. *SPE Reservoir Eng.* **1991**, *6*(1), 17−24.

(62) Monger, T. G. *Phase Behavior Studies of Appalachian Crudes with Carbon Dioxide*; Final Report, U.S. Department of Energy Report No. DOE/MC/11284-17, November, 1982.