The Effects of Inorganic Solid Particles on Water and Crude Oil Emulsion Stability

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The Effects of Inorganic Solid Particles on Water and Crude Oil Emulsion Stability

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Small inorganic particles strongly enhance water−crude oil emulsion stability when interactions with asphaltenes promote particle adsorption at the oil−water interface. A variety of particle types have been studied to investigate the controlling factors for particle-stabilization effectiveness. Emulsion stabilities were determined by the extent of water resolved after centrifugation and the electric field required for emulsion breakdown. All particles used were hydrophilic and stabilized oil-in-water emulsions if small enough to be interfacially active. When dried and exposed to asphaltene-containing oil phases, the particles stabilized water-in-oil emulsions. Decreased extents of preadsorbed water, decreased particle sizes, and increased particle concentrations enhanced water-in-oil emulsion stability. Investigations with model emulsions showed that an intermediate state of asphaltene aggregation, near the point of incipient precipitation, is required for particle modification and emulsion stabilization. Increased asphaltene−particle interactions increased emulsion stabilization effectiveness.

1. Introduction

Emulsions are found in a variety of industries, from food and pharmaceuticals to petroleum production and refining. Emulsions result from the mixing of two immiscible liquids. One of the liquids, the disperse phase, is distributed as droplets in the other liquid, the continuous phase. Although they are useful for viscosity control, transfer processes, and chemical reactions facilitated by the large interfacial area between two phases,[1,2] emulsions can also be detrimental, as in the petroleum industry.

Water or brine typically accompanies crude oil during its recovery from a reservoir. Additional water might also be added to aid in secondary oil recovery as the well nears the end of production.[3−5] Emulsions form as a result of the presence of water coupled with the application of high shear stresses at the wellhead and choke valves.[6−8] At the refinery, additional water is emulsified in an effort to extract salts and fine solids from the crude oil (Figure 1).[2,9] The presence of the emulsion is beneficial for the extraction process, but it poses major problems for the additional refining steps.[10,11] The accumulation of surface-active molecules and inorganic solids from the crude at the oil−water interface produces a mechanically strong, rigid, viscoelastic stagnant film that resists droplet coalescence.[4,6,9,12−42] If allowed to pass through refinery operations, emulsified water will corrode refinery equipment, such as overhead distillation columns, and poison catalysts as a result of dissolved salts.[7−9,23] The viscous emulsions will foul machinery, and entrained solids will accumulate in certain unit operations. The oil lost and the problems associated with waste disposal make emulsions a major problem for the petroleum industry.[6,8,23,43−45]

This study is aimed at developing a better understanding of emulsion stabilization in the presence of inorganic solid particles. It is hoped that the results will provide information to aid in the production and refining operations of the petroleum industry.

2. Background

2.1. Surface-Active Species in Petroleum. The mechanism for emulsion stabilization in petroleum and petroleum-derived fluids is not completely understood. Many attribute emulsion stability to the viscoelastic interfacial film mentioned previously. This skin is formed through the interactions of the surface-active molecules in the crude, which fall into two main categories, asphaltenes and resins.[27,32,44−46] Asphaltenes are flat sheets of condensed polyaromatic hydrocarbons interconnected by sulfide, ether, aliphatic chain, and naphthenic ring linkages.[47,48] The edges of the sheet consist of alkyl chains. Resins are structurally similar to typical surface-active molecules. One end is hydrophilic, with polar functional groups; the other is hydrophobic, consisting of alkyl chains. In the nonpolar oil environment, the polar end of the resins interacts with exposed cores of asphaltenes, leaving the nonpolar end of the resins to interact with the crude oil medium. The polar cores of asphaltenes can also interact with polar cores from different asphaltene molecules, producing asphaltenic aggregates solvated with resins. These aggregates have been observed with X-ray diffraction, small-angle neutron scattering, and small-angle X-ray scattering to be from 10 to 50 Å in radius.[48−53] The extent of asphaltene aggregation depends on the aromaticity of the crude oil medium and the resin composition. The colloidal aggregates can be interfacially active if the asphaltenes are in a state of solvation such that the interaction with the interface is energetically favored over interactions with resins and aromatics in the oil phase (poor solvent conditions), but the aggregates have to be small enough to be held at the interface through hydrogen-bonding interactions with the water phase and interfacial tension forces (good solvent conditions). Thus, there is an intermediate extent of solvation at which the formation of a viscous, cross-linked, interfacial network of asphaltenes occurs.[54−58] Figure

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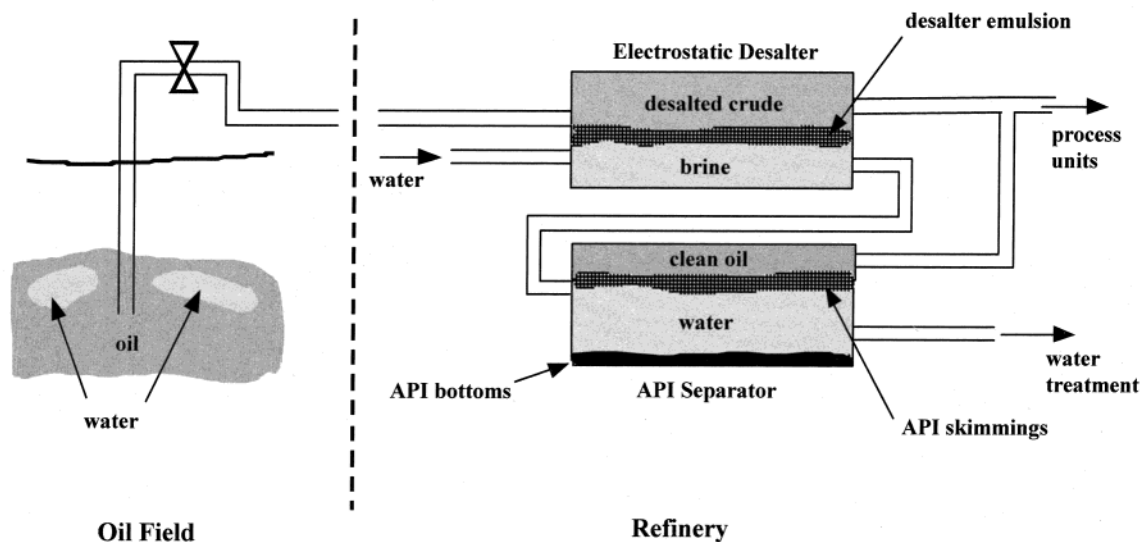
Figure 1. Schematic of petroleum production and refining processes in which emulsions are encountered.
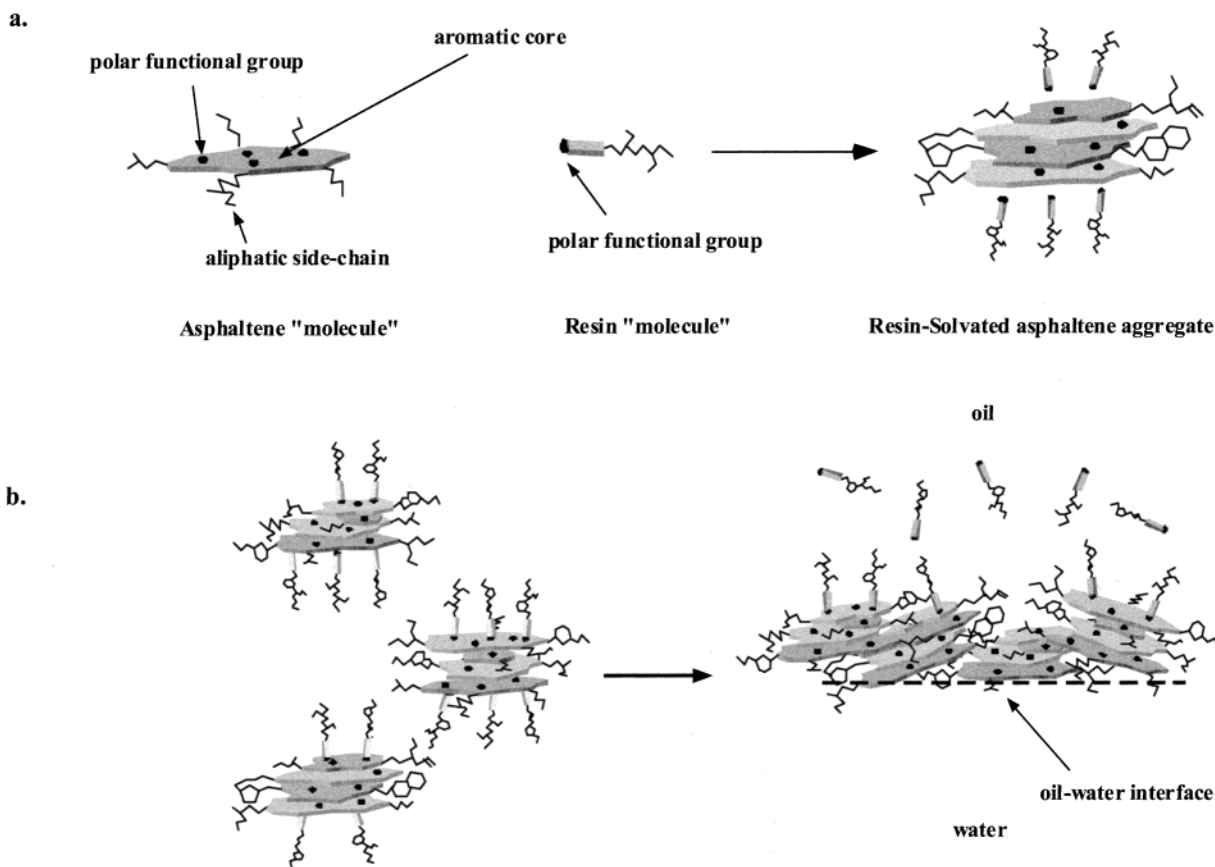
**Figure 2.** (a) Resin−asphaltene association to form a colloidal aggregate. Asphaltenes interact through hydrogen bonding and π-bond overlap. Resins solvate asphaltene aggregates through polar functional group interactions. (b) Resin−asphaltene colloidal aggregate association to form an interfacial film. Primary asphaltene aggregates cross-link to form a rigid, viscoelastic structure at the oil−water interface.

2 illustrates the interactions between asphaltene and resin molecules and their association to form an interfacial film. There are many excellent studies that discuss the role asphaltene and asphaltene−resin interactions play in the stabilization of water-in-oil emulsions.[9,15,16,27,28,44,58−64]

2.2. Particle-Stabilized Emulsions. The presence of inorganic solids can add to emulsion stability if the particle sizes are small enough (a few microns or less) to become interfacially active with the adsorption of resins and asphaltenes from the crude. The presence of particles adds bulk to the interface and increased stability to the asphaltene−resin film.[6,44,65] Illustrations of particle-stabilized emulsions are shown in Figure 3, along with a stabilized water-in-oil emulsion in the absence of solids.
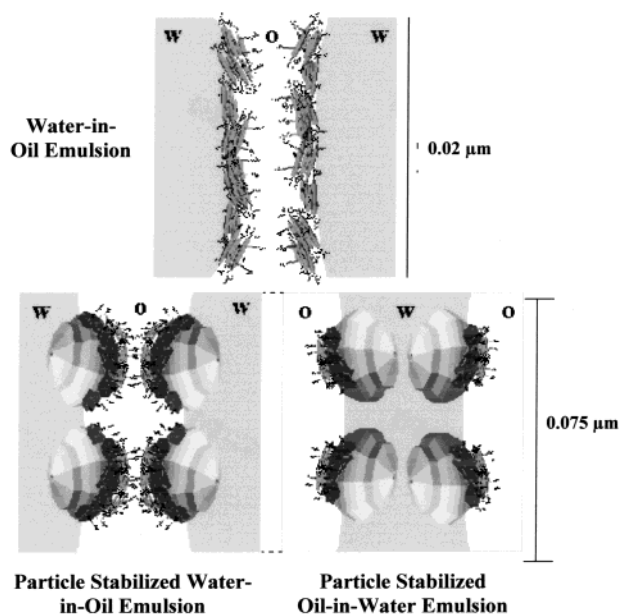
Figure 3. (a) In the absence of particles, water-in-oil emulsions are stabilized by resin/asphaltene films. (b) Inorganic particles sit at the interface, stabilizing water-in-oil emulsions if a sufficient amount of asphaltene aggregates adsorb. (c) The same particles with a lesser extent of asphaltene adsorption will stabilize oil-in-water emulsions. (0.026-μm-diameter particles shown, same as Fe$_2$O$_3$ used in this study)

The existence of solid-stabilized emulsions has been known since the beginning of this century.[66-70] This stabilization occurs when particles are partially wet by both phases. Hydrophilic particles have contact angles less than 90° (measured through the water phase) and stabilize oil-in-water emulsions. Hydrophobic particles have contact angles greater than 90° and stabilize water-in-oil emulsions.[67,70-74] Tambe and Sharma (1993)[75] varied the contact angle of clay particles in an n-decane/water system by adding stearic acid. The acid concentration required to change the contact angle to 90° corresponded with the concentration required for emulsion inversion. A clear dependence of emulsion stability on particle size has also been detected. Schulman and Leja (1954),[74] Kitchener and Musselwhite (1968),[76] and Tambe (1994)[13] all showed an increase in emulsion stability with a decrease in particle size. The effect of particle concentration on emulsion stability has also been studied. Menon and Wasan (1984)[77] added shale dust to shale oil/water systems. Increasing the concentration of particles decreased the coalescence rate of the emulsion. At particle concentrations above those required for monolayer coverage of the interface, coalescence rates decreased significantly with further increases in particle concentration. Gelot et al. (1984)[73] found that an increase in particle concentrations decreased emulsion droplet sizes and increased emulsion volumes, providing more area for interfacial adsorption. Tambe and Sharma (1993)[75] showed an increase in emulsion stability with particle concentration as well.

The studies discussed above investigated the effects of various particle characteristics on emulsion stability in systems with well-characterized "oil" phases. Crude oil is a much more complex mixture, with a large number of chemical species. The variation in chemical content of different crudes is enormous. For example, for the 20 crude oils present in our laboratory, the asphaltene concentration varies from 0.1 to 15%, and the resin content ranges from 3 to 20%. An understand-

ing of the effect of particles on emulsion stability in systems with these components is required to apply results to the petroleum emulsion problem.

Anderson[78] wrote an extensive literature review on the exposure of reservoir rock to various oil and brine systems and the effect on wettability. Interaction of water-wet cores from oil reservoirs with polar components and other organic material from crude oil increases oil wettability of the rock.[79-81] Many studies of the adsorption of asphaltenes onto clay particles and the effect of this adsorption on the three-phase contact angle (solid/water/oil) have been performed. An increase in asphaltene adsorption increases the contact angle, θ, measured through the water phase (increased oil wettability), as shown in Figure 4.[25,82-89] Yan and Masliyah (1994)[90] showed that an increase in the thickness and elasticity of the clay particle layer adsorbed at the oil−water interface occurred in conjunction with this increased contact angle. Marlow et al. (1987)[91] found that increasing asphaltene adsorption leads to increased clay dispersion settling times, suggesting increased interparticle repulsive forces due to adsorbed asphaltenes. These experiments were performed at low asphaltene concentrations (0.04 wt %) and are not surprising given the fact that unmodified clay particles in a hydrophobic environment will rapidly flocculate in response to hydrophilic forces. Yan and Masliyah[92,93] determined the maximum emulsion stability at clay contact angles of 90° for experiments performed with constant concentrations of solids. At this contact angle, the concentration of solids at the interface was the highest. For experiments in which the particle concentration at the interface was constant, emulsion stability decreased with increasing contact angle, as particles were more immersed in the oil phase, providing a smaller barrier to coalescence. Network formation between clay particles at oil droplet interfaces and surfactants in the continuous phase have been observe by X-ray diffraction.[85,94] This network structure was presumed to lead to emulsion stability. Many investigators have studied the role of asphaltene solvency and found it to be the most important parameter for controlling particle wettability.[95-100] Asphaltenes that are more solubilized are better able to modify particle surfaces. The adsorption of resins has been shown to affect the wettability of minerals to a certain extent as well.[88] The adsorption rate constant, as measured by the reduction of the resin concentration in solution with time (spectrophotometrically), was found to be lower than that for asphaltenes. Particles modified with resins showed changes in contact angles, but the particles remained water-wet and stabilized only oil-in-water emulsions. Clementz[85] found a decrease in basic nitrogen content from 0.31 to 0.27% when a heavy ends fraction of petroleum was dissolved in benzene and exposed to sodium montmorillonite, suggesting that basic nitrogen plays a role in asphaltene adsorption. FTIR analyses of asphaltene solutions before and after particle adsorption showed a higher relative intensity and an upward shift of the aromatic C=C stretch in the adsorbed fractions relative to that of whole asphaltenes. Clementz thus concluded that there is selective adsorption of the most aromatic compounds and π-bonding between the asphaltenes and the clay surface. Ion binding of asphaltenes with cations in the clay has been concluded as another type of interaction based on increased adsorption with clays containing cations of higher valences.[85,95]
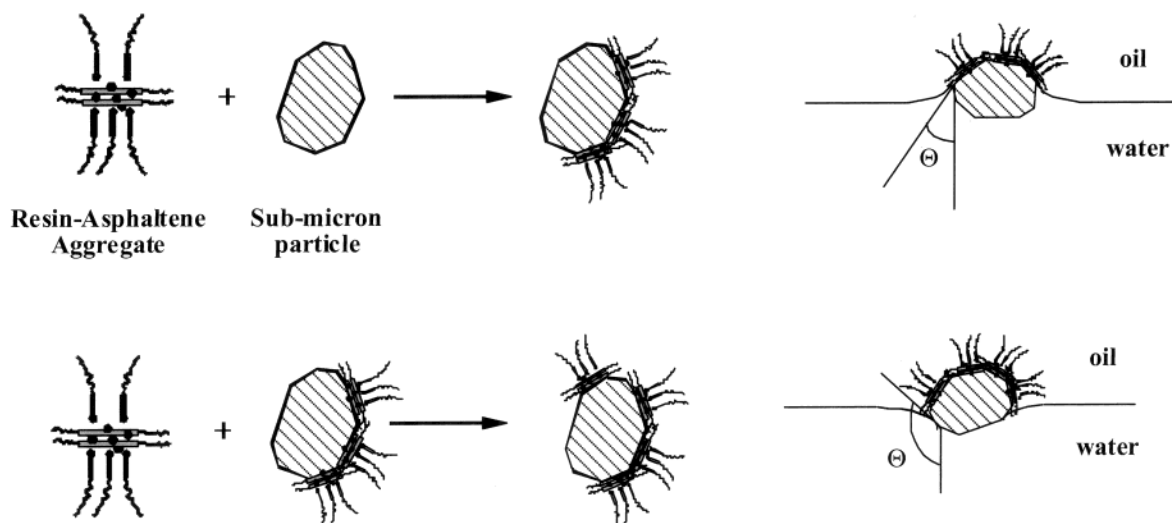
Figure 4. Adsorption of resin/asphaltene aggregates to a hydrophilic particle. At low extents of adsorption, the particle is preferentially wetted by the aqueous phase (Θ < 90°). As more aggregates adsorb, the particle becomes preferentially wetted by the oleic phase (Θ > 90°).

These findings indicate that the change in particle wettability due to adsorption of resins and asphaltenes from the crude oil is the primary reason for the accumulation of particles at the interface. The link between particle modification in the above systems and crude emulsion behavior is still needed for the prediction of crude emulsion stabilization in the presence of inorganic solid particles. How do asphaltene–particle chemical interactions affect stabilization? How does the stabilization effectiveness change with particle concentration or type? To answer these questions, a thorough study with a variety of particles has been undertaken. To better understand how particles control emulsion stability, we need to know the various stabilization mechanisms.

2.3. Mechanisms of Emulsion Stability. Emulsions are stable when the disperse-phase droplets do not coalesce over some time scale or under the influence of a centrifugal field of practical interest. Coalescence occurs in three steps: (1) approach of the droplets through the continuous phase; (2) deformation of the droplets to form a thin film between them; and (3) thinning of this film to a critical thickness, below which the droplets coalesce.[101] There are at least four mechanisms by which emulsions are stabilized: (1) electrostatic repulsion; (2) steric repulsion; (3) the Marangoni–Gibbs effect, which retards film drainage; and (4) thin film stabilization. A brief review of each of these is given below.

2.3.1. Electrostatic Forces. The first step in the resolution of emulsions is the coagulation of disperse-phase droplets, which might be resisted by electrostatic forces. Electrostatic forces do not play a significant role in the stabilization of water-in-oil emulsions because of the low dielectric constant of the continuous phase. Most emulsions formed during petroleum production and refining are oil-continuous because the stabilizing surfactants—asphaltenes and resins—reside in the oleic phase. At the reservoir, crude oil is produced with suspended micron-sized inorganic particles. These particles are hydrophilic and can stabilize oil-in-water emulsions if sufficiently modified with asphaltenes and resins. Particles are also found accumulated in electrostatic desalters and API separators after separation from crude oil. Srivastava[102] performed a study of oil-

in-water emulsions stabilized by 11 different finely dispersed metal hydroxides. He found emulsion stability to be due to the strength of the interfacial film formed around the droplets, not electrostatic forces. This was implied from the observation of a thick interfacial film, and an increased coalescence rate constant when solids were present (10^{-4} s^{-1} compared to 10^{-5} s^{-1} with no solids). Observations of the interfacial films were performed with an optical microscope. Electrostatic forces were found to affect flocculation, but coalescence was the rate-limiting step. These findings indicate that electrostatic forces probably do not influence emulsion stability to a great extent for emulsions stabilized by asphaltenes or inorganic solid particles. Resins and other organic acids can be water-soluble and contribute to oil-in-water emulsion formation, if ionized. In these cases, electrostatics might play a role, but such emulsions were not investigated in this study.

2.3.2. Steric Repulsion. The resistance of adsorbed species on droplet interfaces to interactions with adsorbed species on other droplets is referred to as steric repulsion. Steric repulsion occurs when it is energetically favorable for the adsorbed material to interact with the solvent in the continuous phase rather than other adsorbed material. Under these circumstances, as two droplets approach one another, there is an energy barrier for shedding the solvation shells around the adsorbed species and replacing the associated solvent interactions with interactions from adsorbed species on other droplets. Mackor and van der Waals[103] modeled the adsorption of molecules onto a pair of planes and, by comparing their results with experimental findings, concluded that the energy barrier associated with steric forces was the stabilization mechanism for some dispersions.

Steric repulsion is commonly found in systems stabilized with nonionic polymers where solvation energies can be high as a result of hydrogen-bonding interactions. In water-in-oil emulsions, solvation energies of this magnitude are probably uncommon for resin/asphaltene aggregates adsorbed to water droplets. The solvent in these cases consists of a mixture of saturated and aromatic hydrocarbons. Such species will interact with the adsorbed asphaltene and resin molecules through much weaker van der Waals forces. However, steric

repulsion probably plays a role in the stability of asphaltene dispersions because of the highly energetic resin−asphaltene interactions.

2.3.3 Marangoni−Gibbs Effect. Wasan[10] found that the critical thickness for rupture of a thin film depends on the adsorption kinetics and interfacial activity of added demulsifiers. As the film thins, the continuous phase drains out from between the droplets, and an interfacial tension gradient is formed as the surfactants at the droplet interface are dragged outward with the liquid. Because of the depletion of surfactant at the center of the thin film interface, a diffusion flux is generated in the opposite direction of the drainage, increasing the rigidity of the interface and slowing fluid drainage. This phenomenon is known as the Marangoni−Gibbs effect.[7,22,104] To enhance coalescence, the interfacial activity of the demulsifier must be high enough to account for this interfacial tension gradient.[10,46,104−106] Improved demulsifier performance is observed with increased dynamic interfacial activity and higher demulsifier diffusivities.[10,46] Mukherjee and Kushnick (1988)[22] found that, for effective demulsification, the interfacial shear viscosity and dynamic tension gradient must be lowered. Stable emulsions exist with both high and low interfacial viscosities but the emulsion is more stable at higher values. In regimes of lower interfacial viscosity, the stability depends on the interfacial tension gradients. Further evidence for this film drainage mechanism is that demulsifiers initially in the disperse phase work better than demulsifiers in the continuous phase. Bulk diffusion of the demulsifier to the interface from the disperse phase is faster than diffusion through the continuous phase, against the flow of the draining film.[7] This mechanism of stabilization is unlikely for crude oil systems because, despite the high surface activity of asphaltenes, the interfacial viscosity in asphaltene-containing systems is high as a result of the formation of a viscoelastic film.

2.3.4. Thin Film Stabilization. The formation of a mechanically rigid, viscoelastic, stagnant film around emulsion droplets in crude oil systems provides a physical barrier for droplet−droplet coalescence. Mohammed et al. (1993),[61] using a Langmuir film balance to measure surface pressure versus area curves, found the interfacial dilatational modulus to have high values for low resin-to-asphaltene ratios and low values for high resin-to-asphaltene ratios for a 1/3 xylene−heptane/water system. Strong films made predominantly of asphaltenes with some resins were responsible for stabilizing emulsions against coalescence. In the absence of asphaltenes, stable emulsions were not formed (immediate water separation). Fordedal et al. (1996)[30] studied the importance of resin−asphaltene interactions to emulsion stability in a decane/water system. They found, as did Mohammed et al., that resins alone are incapable of stabilizing emulsions but have a high interfacial activity. Previous studies in our laboratory have shown that resins are capable of stabilizing coarse emulsions but the application of a centrifugal field results in complete separation.[62] Resins adsorb quickly to water droplet interfaces, slowing coalescence and providing adequate time for asphaltenes to adsorb and form a rigid, cross-linked interfacial structure capable of preventing coalescence over long time periods and significant stresses. These results indicate that any factor influencing asphaltene−asphaltene interactions will influence emulsion stability.

McLean et al.[55] investigated the effect of asphaltene solvency on emulsion stability. Asphaltene solvency was controlled by both the aromaticity of the solvent and the resin concentration. Aromatic solvents interfere with asphaltene−asphaltene π-bonding. The elevated nitrogen content (0.8−2.0%) and decreased H/C ratio (1.3−1.6) relative to whole crude oil (% N < 0.5, H/C = 1.7−1.8) suggest that resins can interfere with both hydrogen bonding and π-bond overlap between asphaltenes. The stability of water-in-crude oil emulsions reached a maximum at an intermediate extent of asphaltene aggregation (Figure 5).

Pasquarelli and Wasan (1981)[17] studied the effects of asphaltenes on interfacial activity and the stability barrier to coalescence. The highest-boiling cut of the crude oil yielded a more rigid interface with a brine solution than lower-boiling cuts. There was an increase in rigidity and a decrease in interfacial tension with an increase in the heavy surface-active components of the crude oil. Considering that the highest-boiling cuts contain the asphaltenes, these results are in line with previous ones.

Eley et al. (1987)[32] showed that the amount of demulsifier needed to destabilize an emulsion correlates with the asphaltene content of the oil. As demulsifier was added, interfacial compressibilities increased, and surface tensions decreased. These findings suggest that demulsifiers are more surface-active than asphaltenes, replacing asphaltene interfacial structures with more easily ruptured monolayers.[23,45,107] The amount of demulsifier required for emulsion destabilization was far less than what would have been needed to replace the asphaltene structure completely, suggesting that coalescence begins at weak spots in the asphaltene film caused by demulsifier disruption.

The results of interfacial film studies show the importance of film rheology to emulsion stability. The results of resin−asphaltene interaction studies show that this film rheology is determined by the accumulation of resin/asphaltene aggregates. The presence of inorganic particles has not been considered. Particles can alter the emulsion system by adsorbing asphaltenes and resins and participating in interfacial film development. These effects must be understood for interfacial film results to be applied to particle-stabilized petroleum emulsions.

The purpose of this investigation is to extend the study of emulsions to systems containing inorganic solids and crude oil or crude oil-like phases. This work will provide useful information for the resolution of emulsion problems facing the petroleum industry. The issues to be addressed are the influence of asphaltene aggregation, as controlled by resin concentration and solvent quality, and the effect of solids size, wettability, and surface chemistry on the stabilization effectiveness of the solids in water/oil emulsion systems.

3. Experimental Section

3.1. Materials. Three different crude oils were used in this study, Arab Heavy (AH), Alaska North Slope (ANS), and Hondo (HO), supplied by Mobil, British Petroleum, and Exxon, respectively. Characteristics of these crudes are reported in Table 1. Specific gravities and kinematic viscosities were obtained from the supplier. Asphaltene and resin fractions were obtained with the procedures outlined below. Elemental analyses of the whole crudes as well as the asphaltene and resin
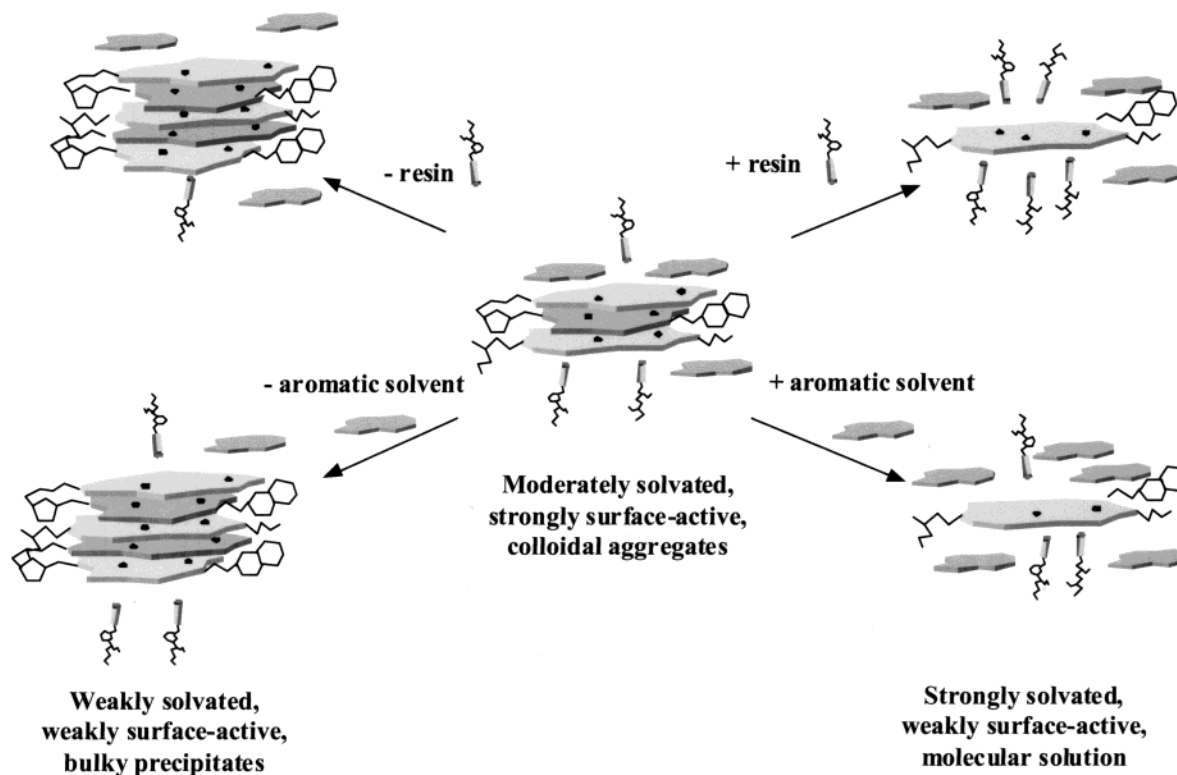
Figure 5. Effects of resin concentration and solvent composition on asphaltene solvency and surface activity. Resins and aromatic solvents disrupt asphaltene aggregation through hydrogen and π-bonding. Increased resin or aromatic solvent content better solvates asphaltene aggregates; elimination of these species encourages asphaltene aggregation.[62]

Table 1. Crude Oil Properties

properties	Arab Heavy (AH2)	Alaska North Slope (ANS)	Hondo (HO)
specific gravity (60 °F)	0.946	0.889	0.938
kinematic viscosity (cSt, 100 °F)	35.7	14.4	387
wt % asphaltene	6.68	3.38	14.81
wt % resin	7.46	8.72	20.52
H/C	1.68	1.71	1.67
asphaltene H/C	1.05	1.06	1.25
resin H/C	1.37	1.41	1.51
asphaltene % N	1.12	1.11	1.96
resin % N	0.88	0.94	1.81

Table 2. Inorganic Solid Particles

material	supplier	average diameter (μm)	density (g/cm^3)	surface area (m^2/g)
Fe$_2$O$_3$	Alfa Aesar	0.026	5.2	44[a]
	Cerac	0.3–0.8	5.2	2.1[a]
Fe$_3$O$_4$	Cerac	0.89	5.2	1.3[a]
Ca(OH)$_2$	Alfa Aesar	16.65	2.2	0.16[a]
kaolin	Aldrich	0.35	2.6	26[b]
montmorillonite	Aldrich	1.45	2.6	6[b]

[a] Calculated from average diameter and density assuming spherical particles. [b] Calculated from average diameter and density assuming disk-shaped particles with 5:1 aspect ratios.

fractions were performed by Galbraith Laboratories (Knoxville, TN). The solvents used for the model oil studies and crude oil fractionation—heptane, toluene, methylene chloride, and acetone—were all HPLC-grade and obtained from Fisher.

The solid particles used are listed in Table 2, along with their suppliers. Ca(OH)$_2$ particles were sized by Particle Characterization Laboratories (NIST, Gaithersburg, MD). The other particle sizes were obtained from the suppliers. Surface areas were calculated from

the average diameter and density values assuming spherical particles for Fe$_3$O$_4$, Fe$_2$O$_3$, and Ca(OH)$_2$ and disk-shaped particles with 5:1 aspect ratios for the two clays. These particles were selected because they are commonly found in refinery emulsions.

3.2. Asphaltene and Resin Fractionation. The fractionation methods have been previously reported elsewhere.[108,109] The asphaltene fraction was isolated by *n*-heptane precipitation. A 40/1 (v/v) *n*-heptane/crude oil mixture was shaken for 24 h at room temperature and then vacuum filtered using Whatman 934-AH filter paper to yield the asphaltene fraction as the precipitate. The precipitate was washed until the filtrate was colorless and then dried in a nitrogen-flushed vacuum oven at 70 °C until the sample reached a constant weight. The heptane from the filtrate was driven off by rotary evaporation at 50 °C to yield maltenes with the volatiles removed.

Resins were obtained by dissolving the maltenes in methylene chloride and adsorbing an aliquot onto 50 g of activated silica gel (Fisher Scientific, chromatographic grade, 35–60 mesh, activated by drying under vacuum at 120 °C for 24 h). After adsorption to silica gel for 24 h, the sample was rotary evaporated at 50 °C to eliminate the solvent and dried in a nitrogen-flushed vacuum oven at 70 °C for 24 h. The adsorbed sample was placed in a chromatographic column and eluted with two solvents. The first solvent, a 68/32 heptane/toluene mixture, eluted the saturate and aromatic fractions. The second solvent, a 40/30/30 acetone/methylene chloride/toluene mixture, eluted the resin fraction. The resins were isolated from the solvent by rotary evaporation at 50 °C, followed by drying in a vacuum oven at 70 °C. Table 1 lists characteristics of the resin and asphaltene fractions of the crude oils that were used

in this study. Resin and asphaltene fraction data from some other crudes are listed for comparison.

3.3. Emulsion Preparation and Stability Testing. 3.3.1. Preparation of Oleic and Aqueous Phases. Prior to use, crude oil was stored in a refrigerator under an argon blanket to prevent oxidation. ANS was used for all crude oil emulsion experiments. Before emulsification, the oil was heated to room temperature and shaken to ensure a homogeneous mixture for sampling. Model oils were a mixture of heptane/toluene, usually 7/3 (v/v), producing a mixture of 74% aliphatic carbon and 26% aromatic carbon on a number basis. Asphaltene and resin fractions were dissolved in the toluene and heptane, respectively, prior to mixing. The asphaltenes were observed to dissolve completely in the toluene. In some cases, solids were added initially to the oleic phase. Adsorbed water on the solids was removed by placing the particles in a nitrogen-flushed Forma Scientific vacuum oven for 24 h. The particles were then removed and immediately transferred to a glovebox. The glovebox was prepared by recirculating argon through it and a drying tube for 1−2 h. Any remaining moisture was absorbed with phosphorus pentoxide. In the glovebox, an Ohaus CT-10 portable balance with a readability of 0.002 g was used to weigh the particles. After particle addition, 24 h passed before any testing was performed to allow for asphaltene and resin adsorption.

The aqueous phase was deionized water (DI) adjusted to pH 6 with HCl and/or NaOH. The water was deionized with Barnstead ROPure LP and NANOpure 4 module systems and adjusted to pH 6 with the addition of 0.05 M HCl and/or NaOH. For the case of particle addition to the aqueous phase, particles were weighed with a Mettler AE166 balance (0.0001 g readability) and added to DI water.

3.3.2. Emulsion Stability Tests. Emulsions were prepared with oil-to-water ratios of 40/60 (v/v). Four milliliters of the oleic phase followed by 6 mL of the aqueous phase were pipetted into 15-mL plastic bottles with a Wheaton adjustable pipet. The oil and water were mixed with a Virtis Virtishear Cyclone IQ Homogenizer, using an internal shaft rotor/stator assembly with a 6 mm diameter and a gap width of 127 μm (0.005 in.). The homogenization was performed between 10 000 and 15 000 rpm for either 2 min at the oil/water interface and 1 min at the bottom of the bottle or 3 min at the oil/water interface and 2 min at the bottom. Homogenization conditions were chosen for emulsions with a spread of water resolved between 0 and 100%. These conditions resulted in emulsion droplet sizes typical of those found in refineries (1−30 μm).[55] After homogenization, the emulsion was poured into a 10-mL plastic centrifugation tube and aged for 24 h.

Emulsions were centrifuged in a Dupont Sorvall RC-5C centrifuge with a fixed-angle rotor for 30 min at 3000 (1060g) or 15 000 rpm (26 600g). The volumes of creamed oil and resolved water were recorded, and the remaining volume of emulsion was calculated by difference. The emulsions were viewed with an Olympus BH-2 polarizing light microscope to determine the approximate droplet size distribution and emulsion type.

An alternative method for measuring emulsion stability is the determination of the critical electric field (CEF) for emulsion breakdown.[30,54,57,58,110−117] This method was used as a check of the water-resolved tests and a clarification of the trends observed in emulsion stability. CEF was measured with a sample cell consisting of two
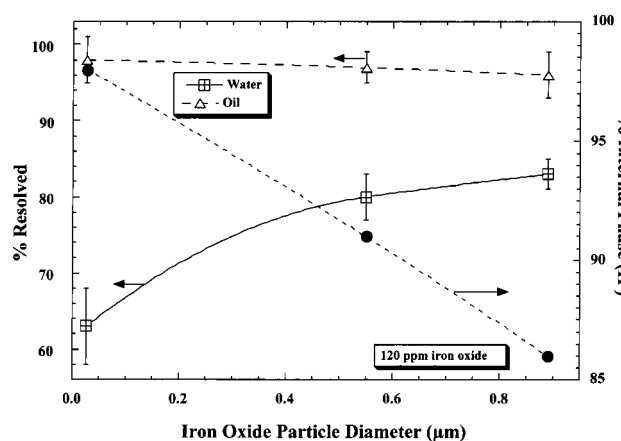
Figure 6. Effect of iron oxide (Fe$_2$O$_3$ and Fe$_3$O$_4$) particle size on water-in-crude oil emulsion stability. Water resolved is the best indicator of emulsion stability because it corresponds to the extent of disperse-phase coalescence.

gold-coated copper electrodes separated by a Mylar spacer. The electrodes were 1.0 cm in diameter and separated by a gap width of 0.25 mm. To test emulsion stability, a small sample (with 1% NaCl in the aqueous phase) was injected into the gap, and the voltage between the electrodes was increased by 0.25 V every 5 s. The current was measured after each voltage change. The voltage control and current measurement were performed with an HP6634B 100-V dc power supply interfaced to a PC and controlled with a Visual Basic program. At low voltages, a small current was measured corresponding to the conductivity of the continuous oil phase. As the voltage was increased, water droplets in the emulsion began to align with the electric field, bridging the gap between the electrodes through the presence of the electrolyte. At a certain electric field strength, the bridging water droplets coalesced to form a continuous water phase between the electrodes, and a large increase in conductivity was observed. In our studies, a jump in current from 0.002 to 0.030 mA was typical as the CEF was reached. More details of this procedure and its implementation for a thorough investigation of crude and model oil systems can be found in Sullivan (2000).[108]

3.4. Solubility Tests. To measure the solubility of asphaltenes under various solvent conditions, 10-mL model oil samples containing 1 wt % asphaltenes were vacuum filtered with Whatman 934-AH glass microfiber filter disks (1.5 μm pore size). After the sample was filtered through the disk, a 10-mL aliquot of the model oil solvent was immediately poured through to rinse any soluble material adsorbed to the microfibers. The rinse step was performed quickly to prevent solubilization of any previously precipitated material. The filtrate was collected, rotary evaporated, and transferred to a small vial. The material remaining on the filter disk was removed with a methylene chloride wash, rotary evaporated, and collected in a separate vial. The filtrate and precipitate vials were dried in a nitrogen-flushed vacuum oven at 70 °C for 2 days and then weighed.

4. Results

4.1. Crude Oil Emulsions. 4.1.1. Addition of Solids to the Oleic Phase. The effect of the iron oxide particle diameter (Fe$_2$O$_3$, 0.026 and 0.55 μm; Fe$_3$O$_4$, 0.89 μm) on ANS crude oil emulsion stability is shown in Figure 6 for a particle concentration of 300 ppm in oil
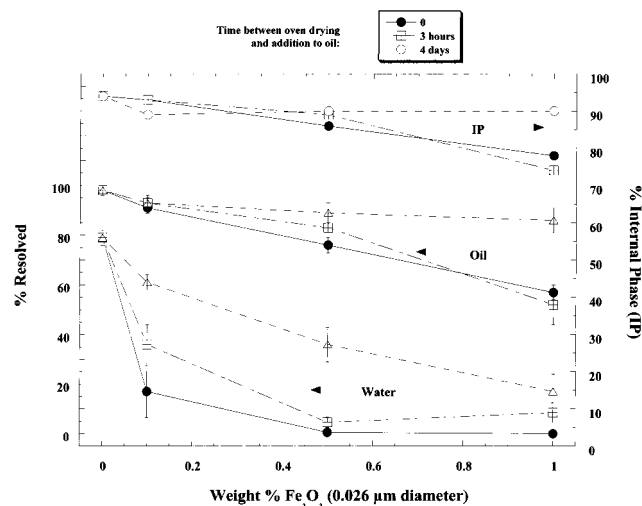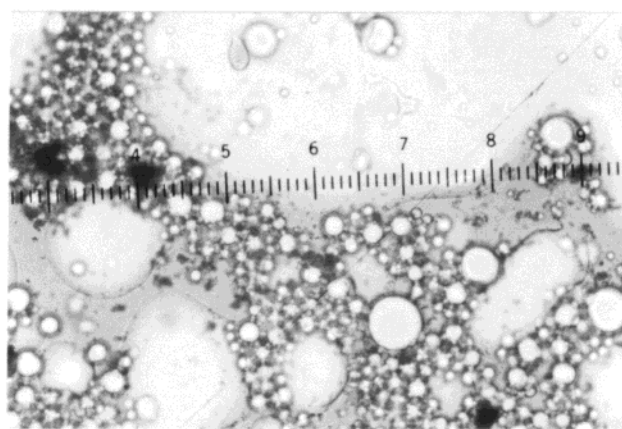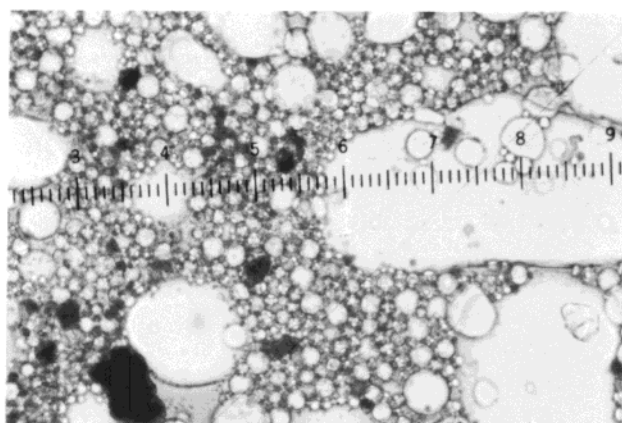
Figure 7. Effect of Fe$_2$O$_3$ particle concentration and surface activity on emulsion stability.

(120 ppm of total emulsion). The crude oil/water mixtures were homogenized for 5 min at 15 000 rpm and centrifuged for 30 min at 15 000 rpm (26 600g). The percentage of water resolved is the best indicator of emulsion stability in this case because it is a measure of the degree of disperse-phase coalescence. An increase in particle diameter from 0.026 to 0.89 μm led to an increase in percentage of water resolved from 63 to 83% with very little change in the amount of oil resolved (which emained near 100). These numbers reflect a water-in-oil emulsion with a high internal phase ratio (97% water for 0.026-μm to 86% water for 0.89-μm iron oxide). The error bars are the standard deviations resulting from 8−10 measured emulsions.

For all remaining tests, emulsions were generated with 3 min of homogenization at 15 000 rpm and tested with 30 min of centrifugation at 3000 rpm (1060g). The centrifugal field was lowered in these subsequent tests because the large density difference between the particles and the liquid phases in the higher centrifugal field (15 000 rpm) resulted in complete emulsion destabilization at all conditions. The effects of 0.026-μm Fe$_2$O$_3$ on emulsion stability are shown in Figure 7 for various lengths of time between the oven drying of particles and their addition to the oleic phase and as a function of particle concentration. Immediately following oven drying, the particles were stored in a desiccator charged with calcium sulfate. Emulsion stability decreased as the time spent in the desiccator by the stabilizing particles increased. We suspect that water preferentially adsorbed to the Fe$_2$O$_3$ rather than the calcium sulfate, reducing the ability of these particles to adsorb asphaltenes and stabilize crude oil emulsions. Emulsion stability increased with increasing particle concentration for all cases, but it rose most dramatically when particles were transferred immediately to the glovebox. These results are in agreement with findings by many investigators.[83,118,119] All further experiments were performed with an immediate transfer from the oven to the glovebox. Microphotographs (Figure 8) for two Fe$_2$O$_3$ concentrations, 0.1 and 0.5% (w/w), illustrate the small, close-packed water droplets. Fe$_2$O$_3$ particles can be clearly seen adsorbed to the surface of the larger droplets. One can also visualize "halos" around the smaller droplets, suggesting that they too are coated with submicron Fe$_2$O$_3$ particles. The large dark patches in Figure 8 are probably aggregated Fe$_2$O$_3$ particles.
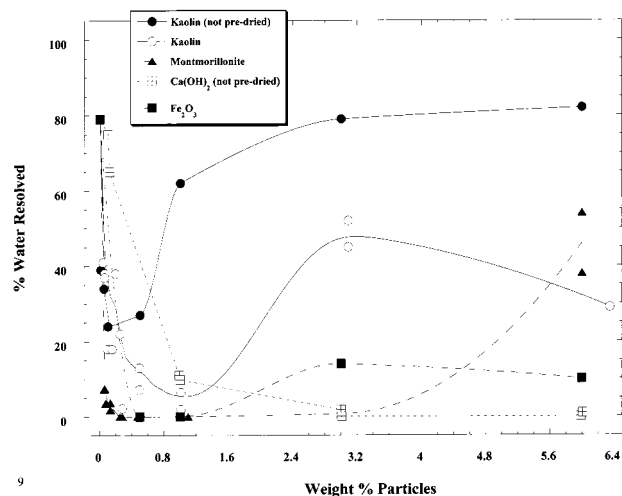

a. 0.1 % Fe$_2$O$_3$

b. 0.5 % Fe$_2$O$_3$

Figure 8. Water-in-ANS crude oil emulsions stabilized with 0.026-μm Fe$_2$O$_3$ (1 division = 3.5 μm).

Figure 9. Effect of concentrations of various particles on water-in-crude oil emulsion stability.

Results for the addition of other inorganic solids to the ANS crude oil phase are shown in Figure 9. The effect of predrying of the particles was again observed with kaolin. The additions of kaolin and montmorillonite had similar effects. The emulsion systems were completely stable to the centrifugal field up to a certain weight percent of particles. After centrifugation, black solid particles were found at the bottom of the water phase in the vials with significant water separation. These results suggest that destabilization at a high

weight percentage of inorganic particles is a result of asphaltene depletion from the oil phase after particle adsorption. If we assume an asphaltene molecular weight of 1000 g/mol, [40,120–127] a molecular radius of 15 Å, columnar asphaltenic aggregates of five molecules, [48] and 10% asphaltene adsorption (estimate based on interfacial film studies of asphaltene adsorption to oil–water interfaces by Spiecker and Kilpatrick, to be published), the surface area covered can be calculated as

$$[(4 \text{ mL ANS})(0.889 \text{ g/mL})(3.4 \text{ wt \% A/100})$$
$$(0.1 \text{ A adsorbed/A})(6.022 \times 10^{23} \text{ molecules/mol})]/$$
$$[(1000 \text{ g/mol})(5 \text{ molecules/stack})] = 3.6 \times 10^{17} \text{stacks}$$
$$(1)$$

$$(3.6 \times 10^{17} \text{stacks})[\pi(7.5 \times 10^{-10} \text{m/stack})^2] = 0.64 \text{ m}^2$$

This area corresponds to 0.25 wt % kaolin and 1 wt % montmorillonite (assuming clay particles are disk-shaped with a 5:1 aspect ratio). These values are within the same order of magnitude as the concentration at which destabilization occurred. Considering the approximate nature of the calculations and the assumptions made, this agreement illustrates that asphaltene depletion is a plausible explanation for emulsion destabilization at high particle concentrations. Clearly, emulsions stabilized by inorganic solid particles and asphaltenes combined can be much more stable than those stabilized by asphaltenes alone, but it is necessary that sufficient asphaltenic aggregates be present in solution to fill the interstitial space between solid particles.

At lower particle concentrations, emulsions are stabilized more effectively with montmorillonite than with kaolin. This result can be attributed to differences in the clay structures. Kaolin consists of layers of hexagonal siloxane sheets alternating with octahedral sheets composed of Al^{3+}. Montmorillonite consists of octahedral layers containing aluminum and magnesium sandwiched between tetrahedral siloxane sheets. Cations are present between the montmorillonite unit layers to balance the negative charge on siloxane. Water or other polar molecules intercalate between the layers and expand the lattice structure.[128] Clementz[85] showed, with X-ray diffraction, increased layer spacing due to asphaltene and resin adsorption. He found that the cation exchange capacity decreased by 27% upon the adsorption of asphaltene and by 52% upon the adsorption of a mixture of asphaltenes and resins. From this result, he concluded that the larger asphaltenes adsorb on external sites of the clay whereas the smaller resins cover or impede the entrances to the interlamellar sites. Both kaolin and montmorillonite adsorb asphaltenes through ion binding with their cations, but kaolin will not expand, reducing its capacity to adsorb asphaltenes relative to montmorillonite. Both Fe_2O_3 and $Ca(OH)_2$ significantly increased emulsion stability over a large range in particle concentration. Stability trends with Fe_2O_3 particle concentration do not show asphaltene depletion effects; otherwise, we would have expected destabilization at a very low particle concentration because of the small size. Performing a calculation similar to that done for the clay particles, a 2 wt % Fe_2O_3 dispersion has a surface area of 9600 m², resulting in 0.007% surface coverage. In oil, many Fe_2O_3 particles might agglomerate and not participate in interfacial film stabilization. There is evidence for this in the emulsion photographs of Figure 8, where large agglomerates are
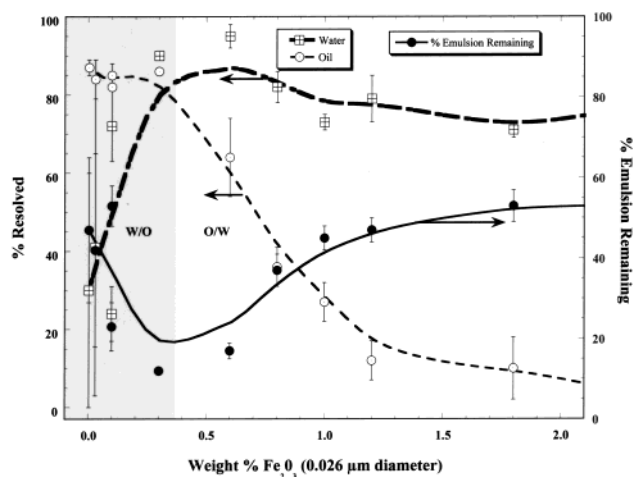

Figure 10. Addition of water-wet Fe_2O_3 particles to ANS crude oil emulsions. The presence of hydrophilic particles inverts water-in-oil emulsions to oil-in-water at high particle concentrations.

seen. Superfine particles have greater ratios of surface to bulk atoms than larger particles, and consequently higher surface energies, increasing the driving force for particle agglomeration. For example the surface energy of a 10-nm copper particle is 9.40×10^{10} erg, 100 times the surface energy of a 1-μm copper particle.[129] The increased stabilization effectiveness of Fe_2O_3 relative to the clays might be due to surface chemistry and higher surface energy. Oxygen atoms on the surface of the Fe_2O_3 particles provide sites for hydrogen bonding with asphaltenes. This bonding, in combination with the high surface energy, might render Fe_2O_3 particles easily modified by adsorption of asphaltenes and hence effective in stabilizing emulsions. Fe_2O_3 that was not pre-dried did not stabilize emulsions at any concentration because all adsorption sites were probably occupied by hydrogen-bonded water molecules. By isolating the Fe_2O_3 from atmospheric water before addition, the adsorption sites were available to interact with asphaltenes. In previous studies,[130] it was found that polar organic solvents with hydrogen-bonding sites have a larger effect on solubilizing asphaltenic aggregates (as gauged by reduced emulsion stability) than solvents that are almost identical but do not contain hydrogen-bond sites. From this finding, we can conclude that asphaltenes are capable of hydrogen-bond formation and surface modification of Fe_2O_3 particles.

$Ca(OH)_2$ particles stabilized emulsions even when not predried and despite their large size. The particle surface energy of $Ca(OH)_2$ is lower than that of Fe_2O_3 so adsorbed water can more easily be replaced by asphaltenes. Unlike Fe_2O_3, $Ca(OH)_2$ is basic, and when suspended in oil, it can strongly interact with acidic species such as carboxylic acids found in asphaltenes. The average size of the $Ca(OH)_2$ particles was much larger than 1 μm, but its low density relative to the other solids studied might have increased the relative stabilization effectiveness in a centrifugal field.

4.1.2. Addition of Solids to the Aqueous Phase. At low concentrations, Fe_2O_3 particles in the aqueous phase stabilized water-in-oil emulsions. Inversion to oil-in-water emulsions occurred at ca. 0.2–0.3% (w/w) solids (Figure 10). At low particle concentrations, there was a wide spread of results, which is indicative of an emulsion in transition from a water-in-oil to an oil-in-water type.
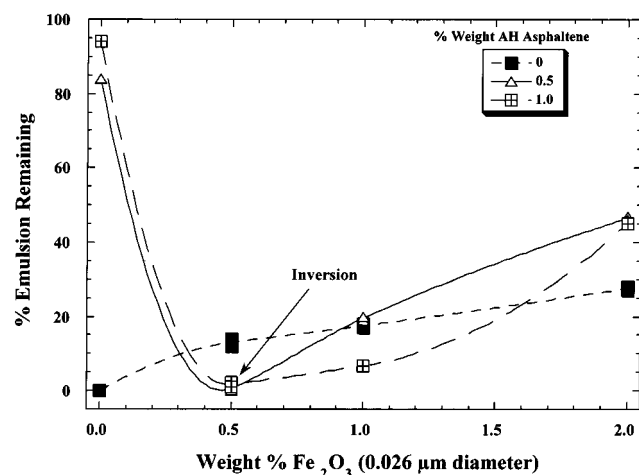
Figure 11. Effect of modification of water-wet particles with low concentrations of asphaltenes on emulsion stability. The particles are made to be more interfacially active, but they remain hydrophilic, stabilizing oil-in-water emulsions.

The results for this set of experiments differ markedly from those in which dried solids were added to the oleic phase. Particles that have been previously modified with adsorbed asphaltenes upon exposure to the oil phase in a water-free environment stabilize predominantly water-in-oil emulsions. In these experiments, by contrast, particles were exposed first to water before contacting the oil phase, significantly reducing the extent of asphaltene adsorption and producing particles that stabilize oil-in-water emulsions. This leads to an inversion from asphaltene-stabilized water-in-oil emulsions at low particle concentrations to solids-stabilized oil-in-water emulsions at higher particle concentrations.

To understand the role of specific oil-phase characteristics in emulsion stability, model oil emulsions were next studied. The use of model oils permits the variation of specific variables such as resin and asphaltene concentration while other factors such as the oil-phase composition and viscosity are kept constant. In this way, we were able to monitor the effects of the resin-to-asphaltene ratio and solvent quality on the emulsion stabilization effectiveness of particles modified by the adsorption of asphaltenes and resins.

4.2. Model Oil Emulsions. In model oil systems with 0.5 wt % asphaltenes, no increased stabilization of water-in-oil emulsions was observed with the addition of predried solid particles. With the addition of the smallest particles—Fe_2O_3 (0.026 μm) or fumed silica (0.014 μm)—an inversion to oil-in-water emulsions was seen with the smallest concentration of added particles (0.5 wt %); with larger particles such as SiO_2 (<2 μm), montmorillonite (1.45 μm), and $Ca(OH)_2$ (16.65 μm), no emulsions were obtained. At this low asphaltene concentration, it was not possible to modify the solid particles to become oil-wet. The solid particles that were too large to adsorb at the oil—water interface did not stabilize emulsions of any kind. Smaller particles were able to adsorb to the interface, but they were not sufficiently surface-modified to become oil-wet and stabilize water-in-oil emulsions. Figure 11 displays data for Fe_2O_3 added to the oleic phase of model systems with low asphaltene concentrations. In the absence of asphaltenes, Fe_2O_3 particles stabilized oil-in-water emulsions. With 0.5% asphaltenes (w/w) and 2.0% Fe_2O_3 (w/w), emulsions were more stable than with Fe_2O_3 particles alone. Apparently, adsorbed asphaltenes from the model
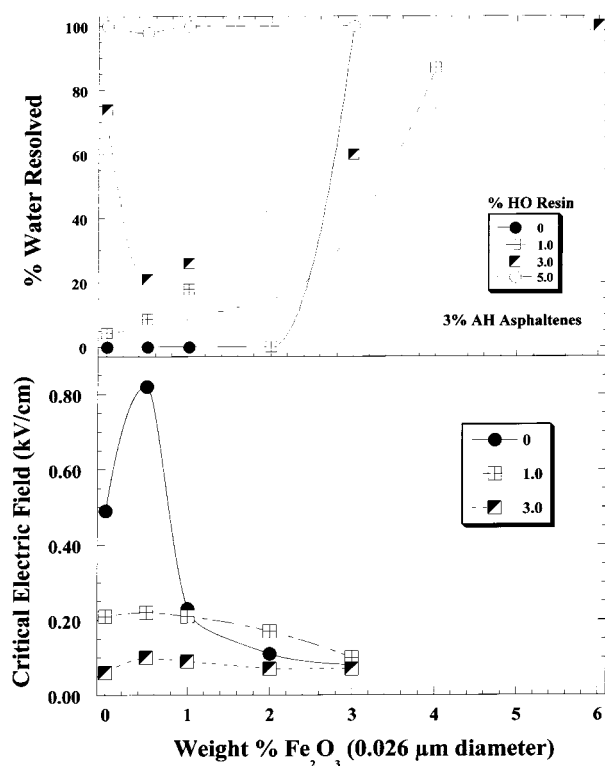
Figure 12. Effect of HO resin concentration on stabilization effectiveness of Fe_2O_3 in 3% AH asphaltene model oil emulsions.

oil made the particles more interfacially active without making them oil-wet, i.e., the contact angle measured through the water was lowered but remained greater than 90°.

Higher concentrations of asphaltenes and resins were used to produce emulsions stabilized by both solid particles and asphaltenes to model crude oil/solid particle systems more closely. Figure 12 illustrates the effect of Fe_2O_3 particles in emulsions with 3% AH asphaltenes at a variety of HO resin concentrations. Emulsion stability was measured by two different methods: percent water resolved and critical electric field (CEF). With no particles, emulsion stability decreased with increasing resin concentration through the solubilization of asphaltenes and the subsequent reduction in the driving force for interfacial adsorption.[30,55] In the absence of resins, an increased particle concentration provided increased emulsion stability up to a certain concentration, followed by decreased stability, as observed with the crude oil studies. This decrease in stability might be the result of particle agglomeration and sedimentation, which has a larger effect here than in crude oil systems because of the lower viscosity of the model oils. Individual Fe_2O_3 particles are small and are held at the interface by adsorbed asphaltenes interacting with the water phase or interfacial material (asphaltenes or particles). At high particle concentrations, particles can agglomerate and form larger structures with entrained asphaltenes and solvent. This agglomeration might be caused by particle bridging due to either adsorbed asphaltene aggregates or the high surface energy of Fe_2O_3. The large agglomerates have a larger sedimentation velocity than the individual particles and require larger forces to hold them at the interface. The equation for sedimentation velocity from Stokes' law is

$$v = \frac{2}{9} \frac{R^2(\rho_2 - \rho_1)g}{\eta} \qquad (2)$$

where v is the sedimentation velocity; R is the particle radius; ρ_1 and ρ_2 are the densities of the particle and solvent, respectively; g is the force acting on the system (gravitational or centrifugal); and η is the viscosity of the solvent. As particles agglomerate, the density of the flocs decreases because of entrained solvent, but their radius increases, resulting in a higher sedimentation velocity because of the squared dependency on the radius. For example, with a model oil viscosity of 0.8 cP and a model oil density of 0.74 g/cm^3, a 0.026-μm Fe_2O_3 particle will settle at 0.079 m/s. In the same solvent, an agglomerate of the same particles with a radius 3 times the individual particle radius and a packing fraction of 0.6 will settle at 0.43 m/s, a rate of over 5 times the individual particle rate.

In general, emulsions produced with resins were less stable than emulsions produced without them. Asphaltenes that were more solvated by resins adsorbed to particles to a lesser extent and had a decreased effect on particle wettability.[85−89,95,98,99] The results for 0, 1, and 3% resins show maximum emulsion stability at ca. 0.5% Fe_2O_3 particles (see CEF results). The increase in emulsion stability with added particles was the most dramatic for model oils with 0% resins. As the asphaltenic aggregates decreased in size with increased resin concentration, their modification of particle wettability decreased. Despite this decrease in effectiveness, the asphaltenes still had some effect on the particles, as shown by the maximum at 0.5% Fe_2O_3 at 3% resins with regards to both percent of water resolved and CEF. Emulsions were stable at higher particle concentrations with 3% resins because better-solvated asphaltene aggregates might have a lower tendency to bridge particles and cause agglomerates to form. At 5% resin, the asphaltenes were well-solvated, and their driving force for adsorption was low. Under such conditions, the particles were not sufficiently modified to stabilize emulsions. These findings indicate that the solubility and surface activity of asphaltenes in the oil phase dictate the effectiveness of stabilization of emulsions by inorganic particles.

Destabilization at high concentrations (3−6% w/w) of Fe_2O_3 particles was not observed when ANS crude was the oleic phase (Figure 9). Apparently ANS was a better dispersant for the particles and reduced particle bridging and consequent agglomeration through the high degree of asphaltene solvation. It is useful to recall that the asphaltene and resin concentrations in ANS are 3.4 and 8.7% (w/w), respectively. Even if particles were to agglomerate, the increased viscosity and density of ANS relative to Heptol would reduce the sedimentation velocity. The sedimentation velocities of an individual Fe_2O_3 particle and an agglomerate (see assumptions above) are 0.0048 and 0.026 m/s, respectively, in ANS, 3 times less than those found in Heptol.

To better understand the role of asphaltene solubility in the solids stabilization process, the solubility of AH asphaltenes in a 70% heptane/30% toluene mixture were measured as a function of HO resin concentration (see Figure 13). Solubility varied from 57.4% with no resins to 88.1% with 3% HO resins. The condition that provided the greatest effectiveness in emulsion stabilization with both solids and asphaltenes was with 57.4% soluble asphaltenes (0% resin). Additional experiments were
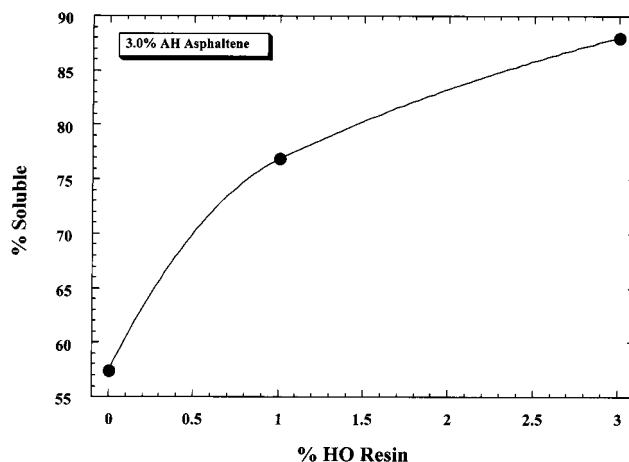
Figure 13. Effect of HO resin concentration on the solubility of 3% AH asphaltenes in 70/30 heptane/toluene.
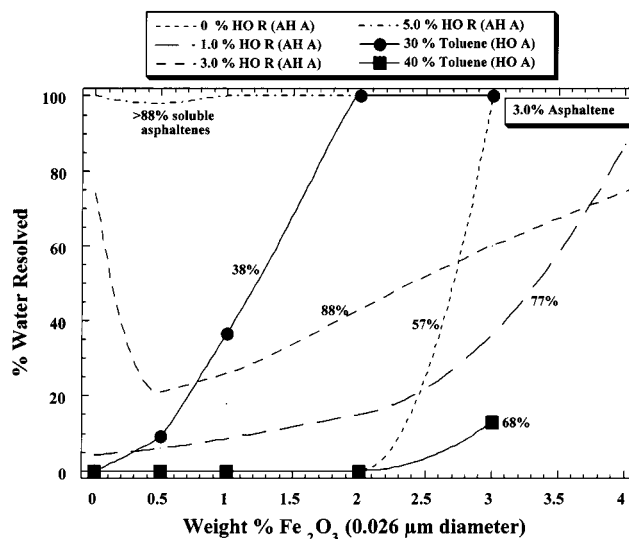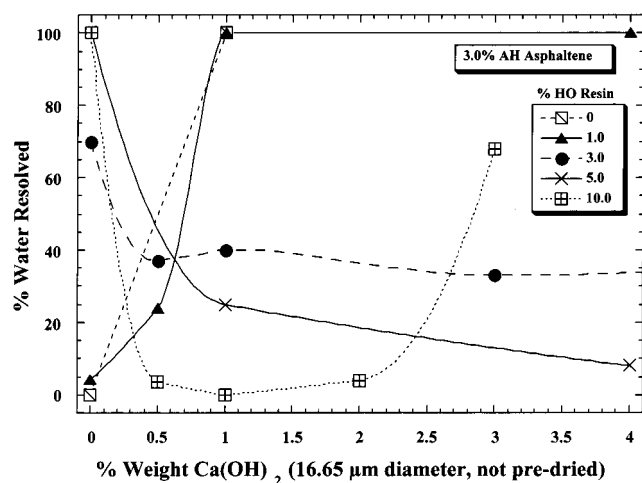

Figure 14. Particle stabilization effectiveness of Fe_2O_3 under various asphaltene solubility conditions.

performed with HO asphaltenes and Fe_2O_3 in which the asphaltene solubility was controlled by the ratio of heptane to toluene rather than by resin concentration. Solubility tests have shown that, at 30 and 40% toluene, HO asphaltenes are 38 and 68% soluble, respectively. Figure 14 shows the stabilization effectiveness of Fe_2O_3 in 30 and 40% toluene with the previously reported results (from Figure 12). At 38% soluble HO asphaltenes, Fe_2O_3 was less effective at stabilizing emulsions than at 57% soluble AH2 asphaltenes. The results for the 68% soluble HO condition are similar to those for the 77% soluble AH asphaltene case. Particle stabilization effectiveness results are similar for similar solubility conditions despite the different asphaltene types and different methods of controlling asphaltene solubility (resin concentration or heptane/toluene ratio). This suggests that the solvation of asphaltenes by resins does not directly affect the ability of asphaltenic aggregates to adsorb onto inorganic solid particles and modify their wettability in the stabilization of emulsion interfaces, but that the solubility and nearness to precipitation of the asphaltenic aggregates dominate this physical process.

The results in Figure 14 illustrate that asphaltenes are most effective at modifying particles and stabilizing emulsions when they are on the verge of precipitating

Figure 15. Effect of HO resin concentration on the stabilization effectiveness of Ca(OH)$_2$ in a 3% AH asphaltene model oil emulsion.

**Table 3. Effect of Ca(OH)$_2$ Particles at Various pH's[a]**

pH	% WR[b] (no particles)	% WR[b] [1 wt % Ca(OH)$_2$]
4	60	12
6	70	40
10	100	20

[a] Heptol, 3% AH A, 3% HO R. [b] Percentage of water resolved.

or are "slightly" precipitated. Under these conditions, asphaltenes are solvated enough to minimize particle bridging, and the concentration of asphaltene aggregates with a sufficient driving force for adsorption is high enough to modify a significant concentration of solid particles (3−4 wt %).

Figure 15 summarizes the findings of Ca(OH)$_2$ particle stabilization studies. Again, as observed for Fe$_2$O$_3$, the solubility state of the asphaltenes is the dominant factor in solid stabilization effectiveness. However, unlike the results for Fe$_2$O$_3$, the solubility range of maximum effectiveness occurs at a high concentration of resin. With 0 and 1% HO resin, emulsions were destabilized with the addition of any Ca(OH)$_2$. Ca(OH)$_2$ particles have a lower surface area than Fe$_2$O$_3$ particles, resulting in thicker adsorbed layers of asphaltene aggregates for the same solubility conditions. As a result, particle bridging destabilizes emulsions at a lower particle concentration than for Fe$_2$O$_3$. Also, the larger size of Ca(OH)$_2$ particles might result in less surface activity at lower extents of particle bridging because of a large particle radius and subsequently higher sedimentation velocities. Ca(OH)$_2$ particles are most surface-active at the highest resin concentration (10%), but destabilization occurs at lower particle concentrations because of the small supply of surface-active asphaltene aggregates for these highly soluble conditions.

In addition to size and surface area, Fe$_2$O$_3$ and Ca-(OH)$_2$ particles differ in surface chemistry. Ca(OH)$_2$ particles have hydrogen-bond donor sites, which might increase their interaction with asphaltenes. To test this hypothesis, emulsions of water with various pH values were made with 1 wt % Ca(OH)$_2$ in model oils containing 3 wt % AH asphaltenes and 3 wt % HO resins. The results are displayed in Table 3. At pH 4 and 6, the results were similar, but Ca(OH)$_2$ had a larger effect with pH 10 water. In this case, the water resolved
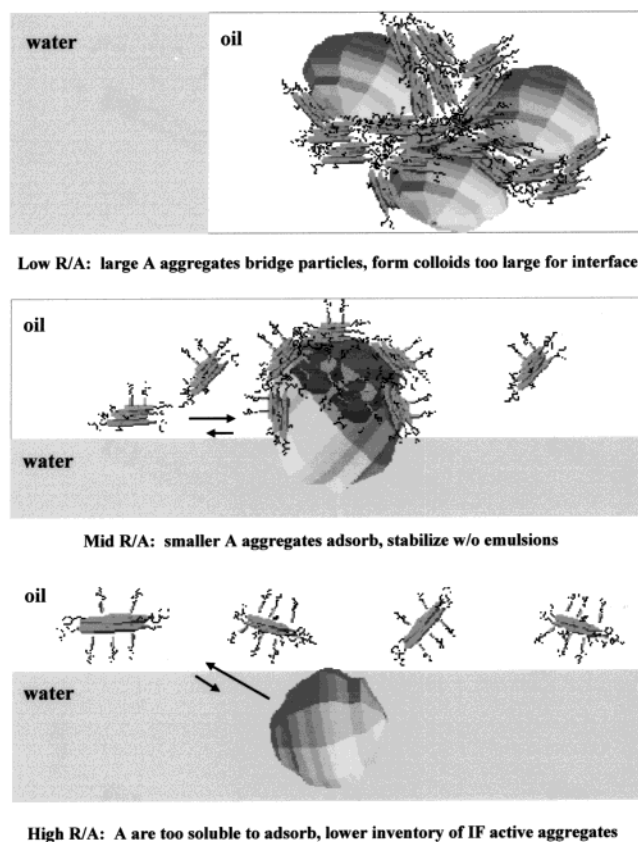

Figure 16. Schematic of resin solubilization of asphaltenes and its effect on particle modification. The state of asphaltene aggregation is a controlling factor for the extent of asphaltene adsorption.

decreased from 100 to 20%. AH asphaltenes do not form an interfacial film stable to coalescence at an interface with basic water and require the presence of hydrogen-bond donors to enhance their interaction with a surface. At pH 10, Ca(OH)$_2$ particle surfaces are more hydroxylated and can donate more hydrogen bonds than at lower pH's, providing an increase in the extent of asphaltene interaction and increased stabilization effectiveness. In addition, resins can become charged and more prone to particle adsorption upon interaction with highly basic water. The relatively large Ca(OH)$_2$ particles require high interaction energies with the oil phase to remain at the interface. These energies can be provided by hydrogen bonds.

In summary, the mechanism of solid particle stabilization in crude oil systems is illustrated in Figure 16. Assuming all crude oil "solvents" are roughly equivalent in H/C ratio, asphaltene solubility is dictated by the R/A ratio. At low R/A, large asphaltene aggregates form thick interfacial films, bridging particles (under less soluble conditions, aggregates might settle out of solution rather than adsorb at all) and preventing adsorption to water−oil interfaces because of the large mass or bulky shape. At higher R/A, smaller asphaltene aggregates adsorb to the particles, conferring interfacial activity and producing particle-stabilized emulsions. As R/A is increased further, the driving force for asphaltene adsorption to the particles decreases, and the inventory of aggregates that are surface-active decreases, making the depletion of asphaltene aggregates through adsorption to the particles a factor in emulsion stability.

To compare the model oil results directly with the results of a crude oil system, Figure 17 shows the effect
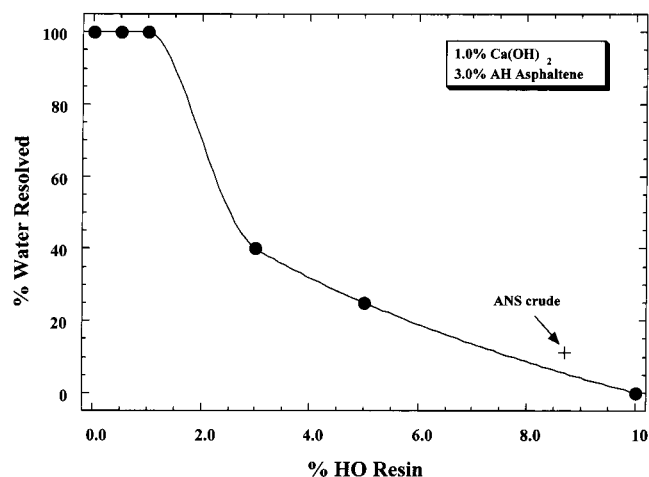
Figure 17. Effect of HO resin addition to 3% AH asphaltene model oil emulsions stabilized with 1 wt % Ca(OH)$_2$.

of adding HO resins to a 3% AH asphaltene system with 1% Ca(OH)$_2$ particles. The percent of water resolved for ANS (3.4% asphaltene, 8.7% resin) with 1% Ca(OH)$_2$ particles is also shown. ANS asphaltenes are similar to AH in H/C ratio and would be expected to have the same solubility as AH in Heptol. The emulsion stability found for the crude oil/particle system is predicted based on the model oils with similar asphaltene and resin concentrations. Thus, particle-stabilization effectiveness in crude oil emulsions is dictated by the solubility of the asphaltene aggregates.

All of these findings suggest a scenario in which the asphaltene molecules exist in a certain state of aggregation based on the solvency of the crude medium, controlled by the ratio of aliphatic to aromatic components as well as the concentration of resins. The state of aggregation determines the amount of asphaltene aggregates that fall within the size limitations for particle stabilization.

5. Conclusions

The effect of the size, concentration, and type of inorganic solid particles on crude oil emulsion stability has been shown. A decrease in the size of oil-wet particles results in an increase in water-in-oil emulsion stability. Hydrophilic particles stabilize oil-in-water emulsions if they are small and their surfaces are not modified, but they stabilize water-in-oil emulsions if dried and added to an asphaltene-containing oleic phase. The effectiveness of water-in-oil emulsion stabilization decreases with increasing preadsorbed water. Inorganic particles present in crude oil reservoirs can become hydrophobic because of the long-term exposure to the crude in the absence of water.

Montmorillonite and kaolin both stabilize water-in-crude oil emulsions effectively when predried. Despite its larger size, montmorillonite stabilizes emulsions more effectively than kaolin because it can swell, increasing its interaction with asphaltenes by exposing interlamellar adsorption sites. Both Fe$_2$O$_3$ and Ca(OH)$_2$ particles stabilize water-in-oil emulsions as well. Ca-(OH)$_2$ has a larger stabilization effect in emulsions produced with basic water, in which the particle surfaces were protonated. This indicates that asphaltenes interact more strongly with hydrogen-bond-donating sites and seems appropriate given the ester, ether,

carbonyl, and pyridine functional groups commonly reported in asphaltenes.

The similarity of the effects of inorganic solid particles in crude and model oil emulsion systems is a good indicator that resin and asphaltene fractions are responsible for the effectiveness of solid particles in crude oil emulsion stabilization. The effectiveness of solid stabilization of water-in-oil emulsions is dictated by the extent of asphaltene aggregation. Aggregation can be controlled with the aromatic/aliphatic ratio of the solvent or the concentration of resin. We have shown that the extent of asphaltene aggregation is the dominant factor for controlling solid stabilization effectiveness.

The first step in the development of a predictive mechanistic model for emulsion stability is the determination of the parameters important for emulsion stabilization. For emulsions encountered in the petroleum industry, some possible parameters are the size and surface energy of the stabilizing particles and the state of asphaltene aggregation. With this study, we have investigated how these variables affect inorganic solid-stabilized emulsions.

Literature Cited

(1) Schubert, H.; Armbruster, H. Principles of Formation and Stability of Emulsions. *Int. Chem. Eng.* **1992**, *32*, 14.

(2) Menon, V. B.; Wasan, D. T. A Review of the Factors Affecting the Stability of Solids-Stabilized Emulsions. *Sep. Sci. Technol.* **1988**, *23*, 2131.

(3) Staiss, F.; Bohm, R.; Kupfer, R. Improved Demulsifier Chemistry: A Novel Approach in the Dehydration of Crude Oil. *SPE Prod. Eng.* **1991**, 334.

(4) Kimbler, O. K.; Reed, R. L.; Silberberg, I. H. Physical Characteristics of Natural Films Formed at Crude Oil–Water Interfaces. *SPE J.* **1966**, 153.

(5) Strassner, J. E. Effect of pH on Interfacial Films and Stability of Crude Oil–Water Emulsions. *J. Pet. Technol.* **1968**, *20*, 303.

(6) Blair, C. M. Interfacial Films Affecting the Stability of Petroleum Emulsions. *Chem. Ind.* **1960**, 538.

(7) Shetty, C. S.; Nikolov, A. D.; Wasan, D. T. Demulsification of Water in Oil Emulsions Using Water Soluble Demulsifiers. *J. Dispersion Sci. Technol.* **1992**, *13*, 121.

(8) Mohammed, R. A.; Bailey, A. I.; Luckham, P. F.; Taylor, S. E. Dewatering of Crude Oil Emulsions 1. Rheological Behavior of the Crude Oil–Water Interface. *Colloids Surf. A: Physicochem. Eng. Aspects* **1993**, *80*, 223.

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

(10) Wasan, D. T. Destabilization of Water-in-Oil Emulsions. In *Emulsions—A Fundamental and Practical Approach*; Sjoblom, J., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; p 283.

(11) Jones, T. J.; Neustadter, E. L.; Whittingham, K. P. Water-in-Crude Oil Emulsion Stability and Emulsion Destabilization by Chemical Demulsifiers. *J. Can. Pet. Technol.* **1978**, *17*, 100.

(12) Urdahl, O.; Sjöblom, J. Water-in-Crude Oil Emulsions from the Norwegian Continental Shelf. A Stablization and Destabilization Study. *J. Dispersion Sci. Technol.* **1995**, *16*, 557.

(13) Tambe, D. E.; Sharma, M. M. The Effect of Colloidal Particles on Fluid–Fluid Interfacial Properties and Emulsion Stability. *Adv. Colloid Interface Sci.* **1994**, *52*, 1.

(14) Tadros, T. F. Fundamental Principles of Emulsion Rheology and Their Applications. *Colloids Surf. A: Physicochem. Eng. Aspects* **1994**, *91*, 39.

(15) Sjoblom, J.; Urdahl, O.; Borve, K. G. N.; Mingyuan, L.; Saeten, J. O.; Christy, A. A.; Gu, T. Stabilization and Destabilization of Water-in-Crude Oil Emulsions from the Norwegian Continental Shelf. Correlation with Model Systems. *Adv. Colloid Interface Sci.* **1992**, *41*, 241.

(16) Sjoblom, 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.

(17) Pasquarelli, C. H.; Wasan, D. T. The Effect of Film-Forming Materials on the Dynamic Interfacial Properties in Crude Oil−Aqueous Systems. In *Surface Phenomena in Enhanced Oil Recovery*; Shah, D. O., Ed.; Plenum Press: New York, 1981; p 237.

(18) 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.

(19) Neustadter, E. L.; Whittingham, K. P.; Graham, D. E. Interfacial Rheological Properties of Crude Oil/Water Systems. In *Surface Phenomena in Enhanced Oil Recovery*; Shah, D. O., Ed.; Plenum Press: New York, 1981; p 307.

(20) Neumann, H.-J. Investigations Regarding the Separation of Crude Oil Emulsions. *Petrochemie* **1965**, *18*, 776.

(21) Neumann, H. J.; Paczynska-Lahme, B. Petroleum Emulsions−Properties, Stability and Demulsification. *Chem. Eng. Technol.* **1981**, *53*, 911.

(22) Mukherjee, S.; Kushnick, A. P. *Effect of Demulsifiers on Interfacial Properties Governing Crude Oil Demulsification*; American Chemical Society: Washington, DC, 1988.

(23) Mohammed, R. A.; Bailey, A. I.; Luckham, P. F.; Taylor, S. E. The Effect of Demulsifiers on the Interfacial Rheology and Emulsion Stability of Water-in-Crude Oil Emulsions. *Colloids Surf. A: Physicochem. Eng. Aspects* **1994**, *91*, 129.

(24) Menon, V. B.; Nikolov, A. D.; Wasan, D. T. Interfacial Effects in Solids-Stabilized Emulsions: Measurements of Film Tension and Particle Interaction Energy. *J. Colloid Interface Sci.* **1988**, *124*, 317.

(25) Menon, V. B.; Wasan, D. T. Particle−Fluid Interactions with Applications to Solid-Stabilized Emulsions Part III. Asphaltene Adsorption in the Presence of Quinaldine and 1,2-Dimethylindole. *Colloids Surf.* **1987**, *23*, 353.

(26) McMahon, A. J. Interfacial Aspects of Water-in-Crude Oil Emulsion Stability. In *Emulsions−A Fundamental and Practical Approach*; Sjoblom, J., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; p 135.

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

(28) Mackay, G. D. M.; McLean, A. Y.; Betancourt, O. J.; Johnson, B. D. The Formation of Water-in-Oil Emulsions Subsequent to an Oil Spill. *J. Inst. Pet.* **1973**, *59*, 164.

(29) Graham, D. E.; Stockwell, A.; Thompson, D. G. Chemical Demulsification of Produced Crude Oil Emulsions. In *Chemicals in the Oil Industry*; Ogden, P. H., Ed.; Royal Society of Chemistry: Cambridge, U.K., 1983; p 73.

(30) Fordedal, H.; Schildberg, Y.; Sjoblom, J.; Volle, 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: Physicochem. Eng. Aspects* **1996**, *106*, 33.

(31) Eley, D. D.; Hey, M. J.; Symonds, J. D.; Willison, J. H. M. Electron Micrography of Emulsions of Water in Crude Petroleum. *J. Colloid Interface Sci.* **1976**, *54*, 462.

(32) Eley, D. D.; Hey, M. J.; Lee, M. A. Rheological Studies of Asphaltene Films Adsorbed at the Oil/Water Interface. *Colloids Surf.* **1987**, *24*, 173.

(33) Dunning, H. N.; Moore, J. W.; Denekas, M. O. Interfacial Activities and Porphyrin Contents of Petroleum Extracts. *Ind. Eng. Chem.* **1953**, *45*, 1759.

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

(35) Cratin, P. D. A Quantitative Characterization of pH-Dependent Systems. *Ind. Eng. Chem.* **1969**, *61*, 35.

(36) Christopher, C. A. Fundamentals of Emulsions. In *Proceedings of the Formation and Breaking of Water-in-Oil Emulsions Workshop*; Amoco Production Company: Calgary, Canada, 1993; pp 63−79.

(37) 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: Physicochem. Eng. Aspects* **1994**, *83*, 273.

(38) Bhardwaj, A.; Hartland, S. Dynamics of Emulsification and Demulsification of Water in Crude Oil Emulsions. *Ind. Eng. Chem. Res.* **1994**, *33*, 1271.

(39) Berger, P. D.; Hsu, C.; Arendell, J. P. Designing and Selecting Demulsifiers for Optimum Field Performance Based on Production Fluid Characteristics. SPE Production Eng. 1988, 3:4, 522.

(40) Acevedo, S.; Escobar, G.; Gutierrez, L.; Rivas, H. Isolation and Characterization of Natural Surfactants from Extra Heavy Crude Oils, Asphaltenes, and Maltenes. Interpretation of Their Interfacial Tension−pH Behaviour in Terms of Ion Pair Formation. *Fuel* **1992**, *71*, 619.

(41) Acevedo, S.; Escobar, G.; Gutierrez, L. B.; Rivas, H.; Gutierrez, X. Interfacial Rheological Studies of Extra-Heavy Crude Oils and Asphaltenes: Role of the Dispersion Effect of Resins in the Adsorption of Asphaltenes at the Interface of Water-in-Crude Oil Emulsions. *Colloids Surf. A: Physicochem. Eng. Aspects* **1993**, *71*, 65.

(42) Cairns, R. J. R.; Grist, D. M.; Neustadter, E. L. The Effect of Crude Oil−Water Interfacial Properies on Water−Crude Oil Emulsion Stability. In *Theory and Practice of Emulsion Technology*; Smith, A. L., Ed.; Academic Press: New York, 1974; pp 135−151.

(43) Liem, A. J. S.; Woods, D. R. Review of Coalescence Phenomena. *AIChE Symp. Ser.* **1974**, *70*, 8.

(44) Johansen, E. J.; Skjarvo, I. M.; Lund, T.; Sjoblom, J.; Soderlund, H.; Bostrom, G. Water-in-Crude Oil Emulsions from the Norwegian Continental Shelf Part I. Formation, Characterization and Stability Correlations. *Colloids Surf.* **1989**, *34*, 353.

(45) Sjoblom, J.; Soderlund, H.; Lindblad, S.; Johansen, E. J.; Skjarvo, I. M. Water-in-Crude Oil Emulsions from the Norwegian Continental Shelf Part II. Chemical Destabilization and Interfacial Tensions. *Colloid Polym. Sci.* **1990**, *268*, 389.

(46) Kim, Y. H.; Wasan, D. T.; Breen, P. J. A Study of Dynamic Interfacial Mechanisms for Demulsification of Water-in-Oil Emulsions. *Colloids Surf. A: Physicochem. Eng. Aspects* **1995**, *95*, 235.

(47) Pelet, R.; Behar, F.; Monin, J. Resins and Asphaltenes in the Generation and Migration of Petroleum. *Org. Geochem.* **1985**, *10*, 481.

(48) Yen, T. F. The Colloidal Aspect of a Macrostructure of Petroleum Asphalt. *Fuel Sci. Technol. Int.* **1992**, *10*, 723.

(49) Sheu, E. Y.; Storm, D. A.; Tar, M. M. D. Asphaltenes in Polar Solvents. *J. Non-Cryst. Solids* **1991**, *131−133*, 341.

(50) Sheu, E. Y.; Liang, K. S.; Sinha, S. K.; Overfield, R. E. Polydispersity Analysis of Asphaltene Solutions in Toluene. *J. Colloid Interface Sci.* **1992**, *153*, 399.

(51) Overfield, R. E.; Sheu, E. Y.; Sinha, S. K.; Liang, K. S. SANS Study of Asphaltene Aggregation. *Fuel Sci. & Technol. Int.* **1989**, *7*, 611.

(52) Ravey, J. C.; Espinat, D. Macrostructure of Petroleum Asphaltenes by Small Angle Neutron Scattering. *Prog. Colloid Polym. Sci.* **1990**, *81*, 127.

(53) Bardon, C.; Barre, L.; Espinat, D.; Guille, V.; Li, M. H.; Lambard, J.; Ravey, J. C.; Rosenrurg, E.; Zemb, T. The Colloidal Structure of Crude Oils and Suspensions of Asphaltenes and Resins. *Fuel Sci. Technol. Int.* **1996**, *14*, 203.

(54) Sjöblom, J.; Førdedal, H.; Skodvin, T. Flocculation and Coaescence in Emulsions as Studied by Dielectric Spectroscopy. In *Emulsions and Emulsion Science*; Marcel Dekker: New York, 1996; p 393.

(55) 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.

(56) Minssieux, l. Removal of Asphalt Deposits by Cosolvent Squeeze: Mechanisms and Screening. In *Preprints of the SPE Formation Damage Control Conference*; Society of Petroleum Engineers: Houston, TX, 1998; Paper SPE 39447, p 289.

(57) Mouraille, O.; Skodvin, T.; Sjoblom, J.; Peytavy, J.-l. Stability of Water-in-Crude Oil Emulsions: Role Played by the State of Solvation of Asphaltenes and by Waxes. *J. Dispersion Sci. Technol.* **1998**, *19*, 339.

(58) Fordedal, H.; Midttun, Ø.; Sjöblom, J.; Kvalheim, O. K.; Schildberg, Y.; Volle, J.-L. A Multivariate Screening Analysis of W/O Emulsions in High External Electric Fields as Studied by Means of Dielectric Time Domain Spectroscopy, II. *J. Colloid Interface Sci.* **1996**, *182*, 117.

(59) Eley, D. D.; Hey, M. J.; Symonds, J. D. Emulsions of Water in Asphaltene-Containing Oils 1. Droplet Size Distribution and Emulsification Rates. *Colloids Surf.* **1988**, *32*, 87.

(60) Mingyuan, L.; Christy, A.; Sjoblom, J. Water-in-Crude Oil Emulsions from the Norwegian Continental Shelf Part VI. Diffuse Reflectance Fourier Transform Infrared Characterization of Interfacially Active Fractions from North Sea Crude Oil. In *Emulsions—A Fundamental and Practical Approach*; Sjoblom, J., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; p 157.

(61) Mohammed, R. A.; Bailey, A. I.; Luckham, P. F.; Taylor, S. E. Dewatering of Crude Oil Emulsions 2. Interfacial Properties of the Asphaltic Constituents of Crude Oil. *Colloids Surf. A: Physicochem. Eng. Aspects* **1993**, *80*, 237.

(62) 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.

(63) Sjoblom, J.; Soderlund, H.; Lindblad, S.; Johansen, E. J.; Skjarvo, I. M. Water-in-Crude Oil Emulsions from the Norwegian Continental Shelf: Part II. Chemical Destabilization and Interfacial Tensions. *Colloid Polym. Sci.* **1990**, *268*, 389.

(64) Sheu, E. Y.; Storm, D. A.; Shields, M. B. Adsorption Kinetics of Asphaltenes at Toluene/Acid Solution Interface. *Fuel* **1995**, *74*, 1475.

(65) Menon, V. B.; Nagarajan, R.; Wasan, D. T. Separation of Fine Particles from Nonaqueous Media: Free Energy Analysis and Oil Loss Estimation. *Sep. Sci. Technol.* **1987**, *22*, 2295.

(66) Ramsden, W. Separation of Solids in the Surface-Layers of Solutions and 'Suspensions'. *Proc. R. Soc. (London)* **1903**, *72*, 156.

(67) Pickering, S. U. Emulsions. *J. Chem. Soc.* **1907**, *91*, 2001.

(68) Newman, F. R. Experiments on Emulsions. *J. Phys. Chem.* **1914**, *18*, 34.

(69) Schlaepfer, A. U. M. Water-in-Oil Emulsions. *J. Chem. Soc.* **1918**, *113*, 522.

(70) Finkle, P.; Draper, H. D.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1923**, *45*, 2780.

(71) Briggs, T. R. Emulsions with Finely Divided Solids. *J. Ind. Eng. Chem.* **1921**, *13*, 1008.

(72) Mizrahi, J.; Barnea, E. The Effects of Solid Additives on the Formation and Separation of Emulsions. *Br. Chem. Eng.* **1970**, *15*, 497.

(73) Gelot, A.; Friesen, W.; Hamza, H. A. Emulsification of Oil and Water in the Presence of Finely Divided Solids and Surface-Active Agents. *Colloids Surf.* **1984**, *12*, 271—303.

(74) Schulman, J. H.; Leja, J. Control of Contact Angles at the Oil—Water—Solid Interfaces. *Trans. Faraday Soc.* **1954**, *50*, 598.

(75) Tambe, D. E.; Sharma, M. M. Factors Controlling the Stability of Colloid-Stabilized Emulsions. *J. Colloid Interface Sci.* **1993**, *157*, 244.

(76) Kitchener, J.; Musselwhite, P. The Theory of Stability of Emulsions. In *Emulsion Science*; Sherman, P., Ed.; Academic Press: London, 1968.

(77) Menon, V. B.; Wasan, D. T. Coalescence of Water-in-Shale Oil Emulsions. *Sep. Sci. Technol.* **1984**, *19*, 555.

(78) Anderson, W. G. Wettability Literature Survey Part 1: Rock/Oil/Brine Interactions and the Effects of Core Handling on Wettability. *J. Pet. Technol.* **1986**, *38*, 1125.

(79) Morrow, N. R.; Lim, H. T.; Ward, J. S. Effect of Crude-Oil-Induced Wettability Changes on Oil Recovery. *SPE Form. Eval.* **1986**, *1*, 89.

(80) Morrow, N. R. Wettability and Its Effect On Oil Recovery. *J. Pet. Technol.* **1990**, *42*, 1476.

(81) Rao, D. N.; Girard, M.; Sayegh, S. G. The Influence of Reservoir Wettability on Waterflood and Miscible Flood Performance. *J. Can. Pet. Technol.* **1992**, *31*, 47.

(82) Menon, V. B.; Wasan, D. T. Particle—Fluid Interactions with Applications to Solid-Stabilized Emulsions Part I. The Effect of Asphaltene Adsorption. *Colloids Surf.* **1986**, *19*, 89.

(83) Menon, V. B.; Wasan, D. T. Particle—Fluid Interactions with Application to Solid-Stabilized Emulsions Part II. The Effect of Adsorbed Water. *Colloids Surf.* **1986**, *19*, 107.

(84) Yan, Y.; Masliyah, J. H. Solids-Stabilized Oil-in-Water Emulsions. Scavenging of Emulsion Droplets by Fresh Oil Addition. *Colloids Surf. A: Physicochem. Eng. Aspects* **1993**, *75*, 123.

(85) Clementz, D. M. Interaction of Petroleum Heavy Ends with Montmorillonite. *Clays Clay Miner.* **1976**, *24*, 312.

(86) Gonzalez, G.; Travalloni-Louvisse, A. M. Adsorption of Asphaltenes and Its Effect on Oil Production. *SPE Prod. Facil.* **1993**, 91.

(87) Gonzalez, G. The Adsorption of Asphaltenes and Resins onto Quartz and Feldspar. In *Proceedings of the 21st Intersociety Energy Conversion Engineering Conference*; American Chemical Society: Washington, DC, 1986; p 245.

(88) Gonzalez, G.; Middea, A. Asphaltenes Adsorption by Quartz and Feldspar. *J. Dispersion Sci. Technol.* **1987**, *8*, 525.

(89) Gonzalez, G.; Middea, A. The Properties of the Calcite—Solution Interface in the Presence of Adsorbed Resins or Asphaltenes. *Colloids Surf.* **1988**, *33*, 217.

(90) Yan, N.; Masliyah, J. H. Adsorption and Desorption of Clay Particles at the Oil—Water Interface. *J. Colloid Interface Sci.* **1994**, *168*, 386.

(91) Marlow, B. J.; Sresty, G. C.; Hughes, R. D.; Magajan, O. P. Colloidal Stabilization of Clays by Asphaltenes in Hydrocarbon Media. *Colloids Surf.* **1987**, *24*, 283.

(92) Yan, N.; Masliyah, J. H. Characterization and Demulsification of Solids-Stabilized Oil-in-Water Emulsions Part 1. Partitioning of Clay Particles and Preparation of Emuksions. *Colloids Surf. A: Physicochem. Eng. Aspects* **1995**, *96*, 229.

(93) Yan, N.; Masliyah, J. H. Characterization and Demulsification of Solids-Stabilized Oil-in-Water Emulsions Part 2. Demulsification by the Addition of Fresh Oil. *Colloids Surf. A: Physicochem. Eng. Aspects* **1995**, *96*, 243.

(94) Tsugita, A.; Takemoto, S.; Mori, K.; Yoneya, T.; Otani, Y. Studies on O/W Emulsions Stabilized With Insoluble Montmorillonite—Organic Complexes. *J. Colloid Interface Sci.* **1983**, *95*, 551.

(95) Yan, J.; Plancher, H.; Morrow, N. R. *Wettability Changes Induced by Adsorption of Asphaltenes*; Society of Petroleum Engineers (SPE): Houston, TX, 1997; p 213.

(96) Buckley, J. S.; Takamura, K.; Morrow, N. R. Influence of Electrical Surface Charges on the Wetting Properties of Crude Oils. *SPE Reservoir Eng.* **1989**, *4*, 332.

(97) Buckley, J. S.; Liu, Y. Some Mechanisms of Crude Oil/Brine/Solid Interactions. *J. Pet. Sci. Eng.* **1998**, *20*, 155.

(98) Buckley, J. S.; Liu, Y.; Monsterleet, S. Mechanisms of Wetting Alteration by Crude Oils. *SPE J.* **1998**, 54.

(99) Buckley, J. S.; Liu, Y.; Xie, X.; Morrow, N. R. Asphaltenes and Crude Oil Wetting-The Effect of Oil Composition. *SPE J.* **1997**, *2*, 107.

(100) Buckley, J. S. Wetting Alteration of Solid Surfaces By Crude Oils and Their Asphaltenes. *Rev. Inst. Fr. Pet.* **1998**, *53*, 303.

(101) Zapryanov, Z.; Malhotra, A. K.; Aderangi, N.; Wasan, D. T. Emulsion Stability: An Analysis of the Effects of Bulk and Interfacial Properties On Film Mobility and Drainage Rate. *Int. J. Multiphase Flow* **1983**, *9*, 105.

(102) Srivastava, S. N. Role of Finely Dispersed Solids (Hydroxides of Polyvalent Metals) as Emulsifiers. *Prog. Colloid Polym. Sci.* **1978**, *63*, 41.

(103) Mackor, E. L.; van der Waals, J. H. The Statistics of the Adsorption of Rod-Shaped Molecules in Connection with the Stability of Certain Colloidal Dispersions. *J. Colloid Sci.* **1952**, *7*, 535.

(104) Krawczyk, M. A.; Wasan, D. T.; Shetty, C. S. Chemical Demulsification of Petroleum Emulsions Using Oil-Soluble Demulsifiers. *Ind. Eng. Chem. Res.* **1991**, *30*, 367.

(105) Hirato, T.; Koyama, K.; Tanaka, T.; Awakura, Y.; Majima, H. Demulsification of Water-in-Oil Emulsion by an Electrostatic Coalescence Methodology. *Mater. Trans.* **1991**, *52*, 257.

(106) Malhotra, A. K.; Wasan, D. T. Stability of Foam and Emulsion Films: Effects of the Drainage and Film Size on Critical Thickness of Rupture. *Chem. Eng. Commun.* **1986**, *48*, 35.

(107) Isaacs, E. E.; Huang, H.; Babchin, A. J.; Chow, R. S. Electroacoustic Method for Monitoring the Coalescence of Water-in-Oil Emulsions. *Colloids Surf.* **1990**, *46*, 177.

(108) Sullivan, A. P. Asphaltene Solvency and the Role of Asphaltenes and Solids in Emulsion Stabilization. Ph.D. Dissertation, North Carolina State Univesity, Raleigh, NC, 2000.

(109) McLean, J. D.; Kilpatrick, P. K. Comparison of Precipitation and Extrography in the Fractionation of Crude Oil Residua. *Energy Fuels* **1997**, *11*, 570.

(110) Urdahl, O.; Williams, T. J.; Bailey, A. G.; Thew, M. T. Electrostatic destabilization of water-in-oil emulsions under conditions of turbulent flow. *Chem. Eng. Res. Des.* **1996**, *74*, 158.

(111) Bailes, P. J.; Larkai, S. K. L. Influence of Phase Ratio on Electrostatic Coalescence of Water-in-Oil Dispersions. *Chem. Eng. Res. Des.* **1984**, *62*, 33.

(112) Bailes, P. J. An Electrical Model For Coalescers That Employ Pulsed DC Fields. *Trans. Inst. Chem. Eng.* **1995**, *73*, 559.

(113) Førdedal, H.; Sjöblom, J. Percolation Behavior in W/O Emuslions Stabilized by Interfacially Active Fractions from Crude Oils in High External Electric Fields. *J. Colloid Interface Sci.* **1996**, *181*, 589.

(114) Abubakar, A. I.; Bello, J. O. Enhanced Coalescence of Emulsion in an Electric Field. *Sep. Sci. Technol.* **1991**, *26*, 1329.

(115) Gang, L.; QiongHua, L.; PanSheng, L. Break-down of Liquid Membrane Emulsion under High Electric Field. *J. Membr. Sci.* **1997**, *128*, 1.

(116) Førdedal, H.; Nodland, E.; Sjöblom, J.; Kvalheim, O. M. A Multivariate 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.

(117) Ese, M.-H.; Sjöblom, J.; Førdedal, H.; Urdahl, O.; Rønningsen, H. P. Aging of Interfacially Active Components and Its Effect on Emulsion Stability as Studied by Means of High-Voltage Dielectric Spectroscopy Measurements. *Colloids Surf.* **1997**, *123*–*124*, 225.

(118) Dean, K. R.; Jr., J. L. M. Asphaltene Adsorption on Clay. *Appl. Clay Sci.* **1986**, *1*, 313.

(119) Jeon, Y. W.; Curtis, C. W. Multicomponent Adsorption of Asphalt Functionalities on Silica. *Fuel Sci. Technol. Int.* **1992**, *10*, 697.

(120) Storm, d. A.; DeCanio, S. J.; DeTar, M. M.; Nero, V. P. Upper Bound on Number Average Molecular Weight of Asphaltenes. *Fuel* **1990**, *69*, 735.

(121) McKay, J. F.; Amend, P. J.; Cogswell, T. E.; Harnsberger, P. M.; Erickson, R. B.; Latham, D. R. Petroleum Asphaltenes: Chemistry and Composition. In *Analytical Chemistry of Liquid Fuel Sources*; Advances in Chemistry Series; American Chemical Society: Washington, DC, 1978; Vol. 170, p 128.

(122) Cyr, N.; McIntyre, D. D.; Toth, G.; Strausz, O. P. Hydrocarbon Structural Group Analysis of Athabasca Asphaltene and its GPC Fractions by C-13 NMR. *Fuel* **1987**, *66*, 1709.

(123) Calemma, V.; Iwanski, P.; Nali, M.; Scotti, R.; Montanari, L. Structural Characterization of Asphaltenes of Different Origins. *Energy Fuels* **1995**, *9*, 225.

(124) Ali, L. H.; Al-Ghannam, K. A.; Al-Rawi, J. M. Chemical Structure of Asphaltenes in Heavy Crude Oils Investigated by NMR. *Fuel* **1990**, *69*, 519.

(125) Al-Jarrah, M. M. H.; Al-Dujaili, A. H. Characterization of Some Iraqi Asphalts II. New Findings on the Physical Nature of Asphaltenes. *Fuel Sci. Technol. Int.* **1989**, *7*, 69.

(126) Ali, M. F.; Saleem, M. Asphaltenes in Saudi Arabian Heavy Crude Oil Solubility and Molecular Weights in Hydrocarbon Solvents. *Fuel Sci. Technol.* **1988**, *6*, 541.

(127) Acevedo, S.; Mendez, B.; Rojas, A.; Layrisse, I.; Rivas, H. Asphaltenes and Resins From the Orinoco Basin. *Fuel* **1985**, *64*, 1741.

(128) Otterstedt, J.-E.; Brandreth, D. A. *Small Particles Technology*; Plenum Press: New York, 1998.

(129) Ichinose, N.; Ozaki, Y.; Kashu, S. *Superfine Particle Technology*; Springer-Verlag: London, 1992.

(130) 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.