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Oilfield solids and water-in-oil emulsion stability

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Abstract

Model water-in-hydrocarbon emulsions consisting of toluene, heptane, water, asphaltenes, and native solids were used to investigate the role of native solids in the stability of oilfield emulsions. The solids were recovered from an oil-sands bitumen, a wellhead emulsion, and a refinery slop oil. The solids were clay platelets and fell into two size categories: (1) fine solids 50 to 500 nm in diameter and (2) coarse solids 1 to 10 µm in diameter. Emulsions stabilized by fine solids and asphaltenes were most stable at a 2:1 fractional area ratio of asphaltenes to solids. It appears that when the asphaltene surface coverage is high, insufficient solids remain to make an effective barrier. When the solids coverage is high, insufficient asphaltenes remain on the interface to immobilize the solids. Treatments that weaken the interface, such as toluene dilution, are recommended for emulsions stabilized by fine solids. Emulsions stabilized by coarse solids were unstable at low solids concentrations but became very stable at solids concentrations greater than 10 kg/m^3. At low concentrations, these solids may act as bridges between water droplets and promote coalescence. At high concentrations, layers of coarse solids may become trapped between water droplets and prevent coalescence. Treatments that flocculate the solids, such as heptane dilution, are recommended for emulsions stabilized by high concentrations of coarse solids. It is possible that emulsions containing both types of solids may require more than one treatment, or even process step, for effective water resolution.

Keywords: Solids; Clays; Particle size distribution; Water-in-oil emulsions; Refinery emulsions; Wellhead emulsions; Stabilization mechanisms; Interfacial composition; Destabilization of emulsions

1. Introduction

Water-in-oil emulsions are encountered in the production, processing, and transportation of crude oil and bitumen. These emulsions are usually undesirable because they are more voluminous and viscous than their constituent liquids. They often require chemical and/or heating treatments, since timely separation of oil and water cannot be achieved with gravity settling alone. Persistent emulsion stability is often attributed to a rigid, viscous film that surrounds water droplets and prevents their coalescence [1–6]. Most often the interface is cited as containing surface-active species such as asphaltenes and resins [6–9] and biwettable particles such as the native sands and clays associated with heavy crude oil/bitumen [10–14] or foreign materials such as corrosion products and additives that have become insoluble.

Solids can potentially stabilize an emulsion by adsorbing onto the water/oil interface directly or by adsorbing onto a film already stabilized by a material such as a surfactant. The solids adsorbed on the interface or existing emulsion film can create a steric barrier between adjacent water drops, hindering collision among drops, effective film drainage, and coalescence [15,16]. They can also contribute to the mechanical rigidity and viscosity of the film if a tightly packed network structure is created and there are strong particle–particle interactions [15,17–21]. However, there is also evidence that partial surface coverage by solids also results in stable emulsions [20,22]. If solids are trapped between drops, they may reduce aggregation and creaming/sedimentation of an emulsion phase and further decrease the chances of coalescence [13]. They may also increase the overall emulsion viscosity [21,23–25] and reduce the

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chances of segregation of water and oil. The mechanisms associated with solids-stabilized emulsions and the degree to which solids increase emulsion stability depend on several factors such as particle size, shape and morphology, density, concentration and surface coverage, and wettability.

Usually, solids capable of stabilizing emulsions are in the submicrometer to micrometer range [15,26,27]. The solids associated with oilfield emulsions are generally less than 1 µm in diameter [13]. Bensebaa et al. [28] and Kotlyar et al. [10,11] have identified these oilfield emulsion solids as aluminosilicate clays with diameters of 100 to 200 nm and thicknesses of approximately 10 nm. Sztukowski and Yarranton [29] found that oil-sands clays from coker-feed bitumen varied from 50 to 500 nm with thicknesses of 8 nm.

Generally, emulsion stability increases with decreasing particle size and increasing particle concentration [7,12,15,17,19,30–35]. The dispersed-phase droplet diameter decreases both with increasing solids concentration and with decreasing particle size [15,21,32]. A decrease in the average drop size tends to result in more stable emulsions. Free energy considerations support these observations [36].

Although less well studied, particle density and shape can also be important in emulsion stability. Emulsions created with denser particles are expected to be less stable than those created with less dense particles [30,32]. Tadros and Vincent [16] suggest that asymmetric particles such as bentonite clays are more effective stabilizers than spherical particles. However, there is also evidence suggesting that irregularities on a surface lessen the emulsifying capability of a particle [22]. Sabbagh and Lesser [37] showed that unstable polyethylene/asphalt emulsions contained teardrop-shaped polymer particles and that stable emulsions contained more spherical particles. Cylindrical particles were also observed in the stable emulsions. Yekeler et al. [38] showed that particle morphology can alter wettability and that smooth particles tend to be more hydrophobic.

Wettability is another important factor when the capacity of solids to stabilize emulsions is considered. Hydrophilic particles, i.e., those with a contact angle less than 90°, tend to stabilize oil-in-water emulsions, whereas hydrophobic particles, i.e., those with a contact angle greater than 90°, stabilize water-in-oil emulsions [15,21,28,30,32]. Thermodynamic considerations suggest that the most stable emulsions will result when the contact angle is 90° for very finely divided solids [20,21,26]. Some experimental evidence supports this conclusion [33], although there is also evidence showing maximum stability at angles other than 90° [13,39,40]. These authors have shown that factors such as particle partitioning, surface coverage, and the phase in which the particle is originally dispersed must be considered, in addition to contact angle.

For the case of native solids such as those encountered in oilfield emulsions, particles possess hydrophilic characteristics in the form of exposed aluminosilicate surfaces and hydrophobic characteristics in the form of adsorbed humic and petroleum materials [10,11]. Asphaltenes have been shown to adsorb readily on various surfaces [41–43] and Kotlyar et al. [10] have demonstrated that asphaltene-like material composes the heavy bitumen molecules adsorbed on aluminosilicate clays extracted from Athabasca bitumen.

Besides rendering particles bi-wettable and capable of interfacial adsorption [7,35,40], asphaltenes also lend rigidity to interfaces [44]. Protective coatings or “skins” are thought to be responsible for the mechanical strength of interfaces [4,5,9,45–48]. Recent work has quantified some of these effects and in fact suggested that emulsion stability is due to high elasticity of the interface [49]. Although asphaltenes alone can stabilize emulsions [50], some of the most stable emulsions result when both asphaltenes and solids are used as stabilizers [12,27]. Sztukowski and Yarranton speculated that asphaltenes lend rigidity to interfaces, while solids prevent bridging among water droplets [29].

In this work, an attempt is made to identify how solids stabilize three different oilfield emulsions: a wellhead emulsion, a refinery slop oil emulsion, and an emulsion formed during oil-sands production. Both model systems prepared from solids extracted from these emulsions and the original refinery and wellhead emulsions are examined. The composition of the model water/oil interface is analyzed by calculating the fractional area occupied by asphaltenes and solids. Emulsion stability is assessed in terms of the free water resolution under an imposed destabilization treatment. The properties of the solids, such as size, distribution, and concentration, are considered and related to the observed trends in model and oilfield emulsion stability. As will be seen, two classes of solids are identified, “fine” and “coarse” particles, which result in different stabilization mechanisms. Treatment options geared toward each stabilization mechanism are evaluated.

2. Experimental methods

2.1. Materials

The model emulsions considered in this work consisted of heptane, toluene, water, asphaltenes, and native solids. Reagent-grade *n*-heptane and toluene were purchased from Van Waters & Rogers Ltd. and used in the precipitation of asphaltenes, the extraction of solids, and the preparation of emulsions. Distilled water was supplied by the University of Calgary water plant.

Asphaltenes were precipitated from Athabasca bitumen, a coker-feed bitumen that has been treated to remove most of the large solids and all of the water. Fine oil-sand solids were also obtained from Athabasca bitumen. Coarse solids were obtained from a wellhead emulsion sample from a heavy oil field, supplied by Alberta Energy Company (AEC) Ltd., now EnCana Corporation. Both fine and coarse solids were recovered from a refinery emulsion supplied by Imperial Oil Ltd. (IOL).

2.2. Separation of asphaltenes and solids

Solids co-precipitate with asphaltenes [50,51]. Therefore, unless otherwise stated, asphaltenes and solids were separated from the source bitumens and emulsions in two main steps: (1) the precipitation of asphaltenes and associated solids from the source material; (2) the separation of the solids from the asphaltene–solids. The procedures used for each source material are as follows:

2.2.1. Athabasca bitumen

To precipitate asphaltenes, n-heptane was added to Athabasca bitumen at a 40:1 (cm^3/g) ratio. The mixture was sonicated for 45 min at room temperature and then left to equilibrate for 24 h. After settling, the supernatant was filtered through a Whatman #2 filter paper without disturbing the whole solution. At this point, approximately 10% of the original mixture remained unfiltered. Additional n-heptane was added to this solution at a 4:1 (cm^3/g) ratio of n-heptane to the original bitumen mass. The mixture was sonicated for 45 min, left overnight, and finally filtered using the same filter paper. The dry filter cake is called asphaltene–solids or AS. Table 1 summarizes the asphaltene yield from Athabasca bitumen. Note that two sources of Athabasca bitumen were considered in order to complete all of the desired model emulsion experiments. Athabasca Bitumen 2 has a smaller yield of asphaltenes and slightly smaller solids content than Athabasca Bitumen 1.

To separate the asphaltenes and solids, the asphaltene–solids mixture was dissolved in toluene at a ratio of 100 cm^3 toluene per gram AS. The mixture was sonicated for 20–40 min to ensure complete asphaltene dissolution and solids dispersion. The mixture was allowed to stand for 1 h, after which it was centrifuged at 4000 rpm (1640 RCF) for 6 min. To recover asphaltenes, the supernatant was decanted and the solvent evaporated until only dry asphaltenes remained. The solids remaining in the centrifuge tube before drying are termed "wet" solids. To obtain "dry" solids, the wet solids were dried in a fume hood at 22 °C until the mass was invariant. Table 1 summarizes the solids content of each AS sample. Dry solids were employed for particle size analysis and TEM observations. Fresh wet solids were employed for emulsion stability experiments.

2.2.2. Wellhead emulsion

The wellhead sample obtained from AEC contained 35% water in the form of an emulsion. The water had to be removed prior to the separation of asphaltenes from solids with consistent results. To remove the water, reagent-grade toluene was added to the emulsion in a ratio of 0.6 cm^3/g. The mixture was shaken on a shaker table for 5 min, ensuring the dispersion of the emulsion in the toluene. The diluted mixture was poured into several 12-cm^3 centrifuge tubes. Each tube was capped with a rubber septum and centrifuged for 5 min at 4000 rpm. After 5 min of centrifugation, the mixture separated into a continuous phase and a "rag" layer. The continuous phase contained the bulk of the heavy oil and toluene and contained only 2.5 vol% water (measured with Karl Fischer titration). The rag layer consisted of emulsified water and a small volume of continuous-phase fluid.

Table 1
Composition of AS from Athabasca Bitumen

Component	Bitumen 1 (wt%)	Bitumen 2 (wt%)
Asphaltene–solids (fraction of bitumen)	17.2	15.1
Asphaltenes (fraction of bitumen)	16.4	14.6
Solids (fraction of bitumen)	0.81	0.47
Asphaltenes (fraction of asphaltene–solids)	95.3	96.9
Solids (fraction of asphaltene–solids)	4.7	3.1

The continuous phase was decanted and the toluene was evaporated in a fume hood until the mass was invariant. Asphaltene–solids were precipitated and recovered from the residual bitumen using the technique described above for Athabasca bitumen. This material is termed "continuous-phase asphaltene solids."

The concentrated rag layer was removed from the centrifuge tubes and placed into a 1-L beaker. Heptane was added to the rag in a 40:1 (cm^3/g) ratio. This mixture was sonicated for 45 min and left to settle for 24 h. After settling, the supernatant was filtered through a Whatman #2 filter paper. Additional n-heptane was added to this solution at a 4:1 (cm^3/g) ratio of n-heptane to the original rag mass. The mixture was sonicated for 45 min, left overnight, and then filtered using the same filter paper. Note that the water associated with the rag gradually collected in pools on the drying filter cake and evaporated overnight. The dry filter cake is deemed "rag-layer asphaltene–solids." The asphaltene and solids yields from the continuous phase and rag layer are summarized in Table 2.

2.2.3. Refinery emulsion

The refinery emulsion contained 43 vol% water in the form of an emulsion. However, unlike the wellhead emulsion, the IOL sample destabilized after five minutes of centrifugation at 4000 rpm into four distinct phases: (1) a continuous phase free of water; (2) a rag layer consisting of 51 vol% water; (3) a free water phase; (4) a solids slurry consisting of 48 vol% water. The rag layer and solids slurry made up only 9 and 7 vol%, respectively, of the total emulsion. Note that, on average, approximately 80% of the water was resolved as a free water phase from the IOL emulsion after this initial centrifugation.

Each phase was decanted from the centrifuge tubes. Asphaltene–solids from the continuous phase were precipitated as described for Athabasca bitumen. Since only small volumes of both the rag layer and the solids slurry were recovered from the refinery emulsion, the solids were recovered directly from these samples rather than asphaltenes first being precipitated. Toluene was added to either rag layer or solids slurry in a 25:1 (cm^3/g) ratio. The mixture was sonicated for 20 min and then left to stand for 1 h. After

Table 2
Composition of AS from AEC wellhead emulsion

Component	Continuous phase (wt%)	Rag layer (wt%)	Total (wt%)
Asphaltene–solids (fraction of phase)	16.1	5.1	
Asphaltene–solids (fraction of bitumen)	14.4	3.7	18.2
Asphaltenes (fraction of bitumen)	14.3	2.0	16.2
Solids (fraction of bitumen)	0.17	1.8	1.9
Asphaltenes (fraction of asphaltene–solids)	98.8	53	89.3
Solids (fraction of asphaltene–solids)	1.2	47	10.7

Table 3
Solid yield of each phase of the IOL refinery emulsion

Component	Continuous phase (wt%)	Rag layer (wt%)	Solids slurry (wt%)	Total (wt%)
Solids (fraction of phase)	0.11	1.8	11.8	
Solids (fraction of bitumen)	0.09	0.29	1.7	2.1

settling, the mixture was sonicated briefly for 10 min and then transferred into centrifuge tubes for 6 min of centrifugation at 4000 rpm. The supernatant was decanted and the solids remaining in the centrifuge tubes were allowed to dry until their mass was invariant. The solids yields from the continuous phase, rag layer, and solids slurry are given in Table 3. The asphaltene content was not determined because the yields of both the rag layer and solids slurry were too small. However, the asphaltene–solid yield from the continuous phase was 7.6 wt%. Solids made up 1.7 wt% of the continuous phase asphaltene–solids.

2.3. *Particle shape and size analysis*

Dry solids were examined with a Philips/FEI field emission transmission electron microscope at an accelerating voltage of 200 kV, as described elsewhere [29]. The particle size distribution of dry solids was obtained with a Malvern Instrument Model 2000 Mastersizer particle size analyzer. The detection range of the instrument varies from 0.020 to 2000 µm and all measurements must be performed in an aqueous environment. The solutions were prepared by dispersing 100 to 200 mg of solids in 10 ml of water. This mixture was shaken by hand and sonicated until it appeared to be free of any clumps of solids and all solids had migrated from the air/water interface to the water. The mixture was then introduced into the 2000 Mastersizer apparatus.

2.4. *Emulsion preparation*

Model emulsions were prepared with heptane, toluene, water, and one of either asphaltene–solids, asphaltenes, or a mixture of asphaltenes and wet solids. The procedure for preparing emulsions stabilized by asphaltenes, AS, or recombined mixtures of asphaltenes and solids has been described previously [29,52] and is summarized here briefly. A known mass of asphaltenes and solids was dissolved and dispersed, respectively, in toluene, after which heptane was added to make up a mixture of 25 vol% heptane and 75 vol% toluene (25/75 heptol). The total volume of emulsions was 50 ml. The mixture was sonicated for 5 min after the addition of heptane to ensure mixture homogeneity. Water in a 40 vol% ratio was added dropwise to the hydrocarbon phase while the mixture was homogenized with a CAT-520D homogenizer at 18,000 rpm for 5 min. After 1.5 h of settling, a continuous phase and a concentrated emulsion phase had separated. For the emulsions stabilized by asphaltenes or asphaltenes and fine solids, the drop size distribution did not change during the settling period, nor did any water separate from the emulsion [50]. The drop size distribution did change during the settling period when AEC coarse solids were used as stabilizers, but no free water was observed.

It was found that dried solids were not suitable for emulsion stability experiments. Chen et al. observed that drying the solids extracted from bitumen froth led to a change in the three-phase contact angle between solid tablets, water, and mixtures of heptane and toluene [53]. A change in wettability would change how the solids in an emulsion were distributed between the bulk phases and the interface and hence would likely affect emulsion stability. Fig. 1 compares the free water resolution after 8 h of treatment (see next section) for model emulsions stabilized by Athabasca Bitumen 1 asphaltenes, asphaltene–solids, and asphaltenes and dry or wet solids recombined in their original ratios. The stability trends show that, if dry solids are utilized, the original emulsion stability (free water resolution) cannot be restored whether the solids are dispersed in the continuous hydrocarbon phase or in the aqueous phase. In fact, these solids appear to have no effect on the emulsion stability, since the free water resolution is the same as when only asphaltenes are used as stabilizers. However, if wet solids are used, the resulting emulsions have the same stability as the original emulsion. Therefore, in this work, all the emulsion recombination experiments have been performed with freshly extracted wet solids.

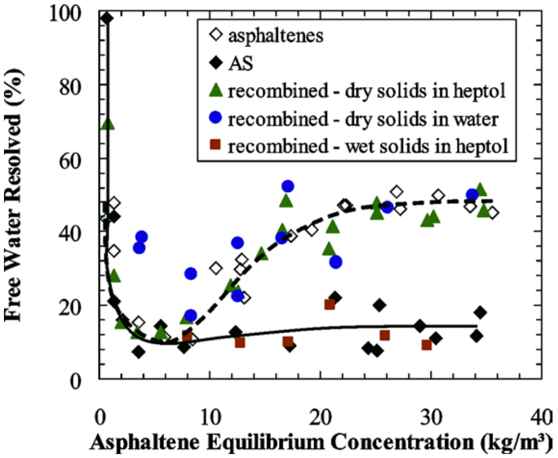

Fig. 1. Emulsion stability after 8 h for (a) asphaltenes, (b) AS, (c) recombined asphaltenes and dry fine solids in heptol, (d) recombined asphaltenes and dry fine solids in water, (e) recombined asphaltenes and wet fine solids in heptol. Athabasca Bitumen 1, 25/75 heptol, 40 vol% water. The lines are visual aids.

2.5. Assessment of emulsion stability

Emulsion stability was gauged by measuring the water resolved from the emulsion as a function of time. After 1.5 h of settling at room temperature, samples of the concentrated emulsion phase were transferred into 12-cm^3 graduated centrifuge tubes and capped to prevent evaporation. The tubes were centrifuged for 5 min at 4000 rpm (1640 RCF) and placed in a water bath maintained at 60 °C. After 2 h, the tubes were removed from the water bath and centrifuged for 5 min and the volume of separated water was measured. The tubes were returned to the heating bath for another 2 h, after which they were centrifuged for 5 min and the free water was measured. This procedure was repeated for a total treatment time of 8 h. The amount of resolved water was reported as the percentage of total water volume contained in the given emulsion sample. The relative stability of all the emulsions was assessed by comparing the percentage of separated water at a given destabilization time.

2.6. Asphaltene and solids surface coverage

Previous studies indicated that for model emulsion systems in which the asphaltene concentration varied from 1 to 40 kg/m^3, asphaltenes adsorbed at the interface as a monolayer [52]. The monolayer mass surface coverage is given by

$$\Gamma_\text{A}^\text{m} = \frac{m_\text{A} d_{32}}{6V_\text{w}}\left(1 - \frac{C_\text{A}^\text{eq}}{C_\text{A}^0}\right), \tag{1}$$

where m_A is the total mass of asphaltenes in the emulsion, d_{32} the Sauter mean diameter of the emulsion droplets, V_w the total volume of the water phase, C_A^eq the asphaltene equilibrium concentration, and C_A^0 the initial asphaltene concentration.

The same procedure can be applied to emulsions containing both asphaltenes and solids, except now, if solids are adsorbed at the interface, the asphaltene surface coverage will be less than the monolayer coverage. The fractional surface coverage of asphaltenes (θ_A) at a water/oil interface was given by the ratio of the asphaltene mass surface coverage to the monolayer mass surface coverage [29]:

$$\theta_\text{A} = \frac{\Gamma_\text{A}}{\Gamma_\text{A}^\text{m}}. \tag{2}$$

For model emulsions stabilized solely by asphaltenes and solids, the solids are assumed to occupy the remainder of the interface, so that the fractional area of solids on the interface, θ_S, is equal to $1 - \theta_\text{A}$.

The variables required to calculate surface coverage from Eq. (1) are the initial asphaltene concentration, C_A^0, the total volume of water, V_w, the Sauter mean diameter, d_{32}, and the asphaltene equilibrium concentration, C_A^eq. The initial asphaltene concentration and the water volume were experimentally controlled parameters. The Sauter mean diameter was found from drop size distributions of samples taken from a settled emulsion. A Carl Zeiss Axiovert S100 inverted microscope equipped with a video camera and image analysis software was used to gather and analyze the drop size distributions. Approximately 400–500 drops were used, giving an expected error of 5–10%, according to Dixon and Massey [54].

The asphaltene equilibrium concentration is determined from a gravimetric analysis of the separated continuous phase. After 1.5 h of settling at room temperature, the continuous phase was decanted from the top of the settled emulsion and its volume measured. The solvent was allowed to evaporate and the residual mass of remaining asphaltenes or asphaltene–solids was determined gravimetrically. For emulsions stabilized solely by asphaltenes, the equilibrium asphaltene concentration is simply the residual mass divided by the volume of the decanted continuous phase. For emulsions containing asphaltenes and solids, the solids in the residual asphaltene–solids mixture were dispersed in toluene at a 100:1 toluene to asphaltene–solids (cm^3/g) ratio and separated using the procedure described for Athabasca bitumen. The mass of asphaltenes remaining after solids removal was then determined gravimetrically and the equilibrium concentration of asphaltenes calculated as before. Note that, for initial asphaltene concentrations less than 10 kg/m^3, the equilibrium concentration was on average 30% smaller than the initial concentration. For initial asphaltene concentrations greater than 10 kg/m^3, the equilibrium concentration was on average 15% smaller than the initial concentration.

The mass of solids in the settled emulsion was determined from a mass balance. For all experiments, the majority of solids were found in the settled emulsion; that is, they had either adsorbed on the water/oil interface or had become trapped between water droplets. No solids were observed in the aqueous phase in any experiment.

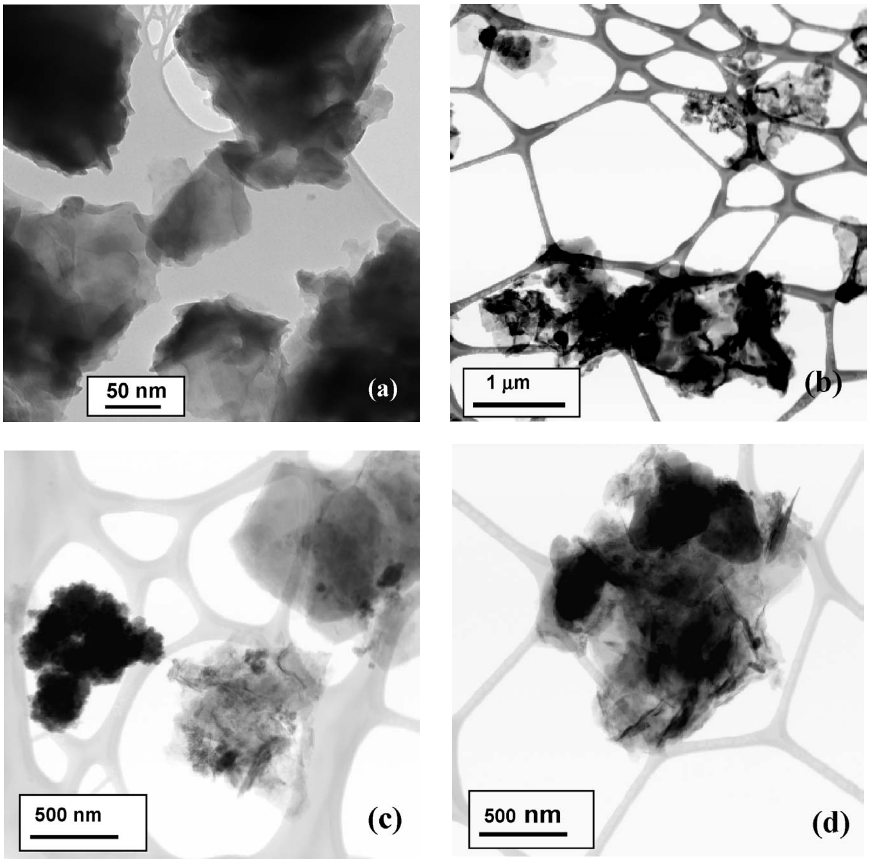

Fig. 2. TEM micrograph of (a) Athabasca oil-sands solids, (b) AEC wellhead solids, (c) IOL refinery rag-layer solids, and (d) IOL refinery solids-slurry solids. Solids are dispersed on carbon webbing.

3. Results and discussion

We first review the source emulsions and characterize the solids from each emulsion. Two types of solids are identified and the role of each type of solid is then investigated using model emulsions. The stability of the model emulsions is compared with the original emulsion as a check on the approach. Finally, the appropriate choice of treatment methods for emulsions stabilized by asphaltenes and solids is discussed.

3.1. The source emulsions and their solids

3.1.1. Coker-feed bitumen

It has been well established that the bitumen product from Syncrude's froth treatment process contains approximately 1 to 3 vol% water in the form of droplets less than 10 µm in diameter [9,10,12,53,55]. This emulsion may be at least partially stabilized by solids and survives centrifugation at process temperatures. After naphtha recovery, these solids remain in the product coker feed bitumen, making up approximately 0.4 to 0.5 wt% of the bitumen [10,12,53]. The froth treatment product stream was not available for testing of the emulsion's stability, but the solids were recovered from the coker-feed bitumen for model emulsion tests.

The extracted solids were analyzed in previous work [29]. As shown in Fig. 2a, they are irregular-shaped clay platelets varying in diameter roughly from 50 to 500 nm and with a thickness of approximately 8 nm. These results were consistent with TEM observations of bitumen solids and mature fine tailings made by others [10,28,56]. They were also consistent with the particle size analysis, Fig. 3, which indicated that 90% of solids were less than 300 nm.

3.1.2. Wellhead emulsion

The AEC wellhead emulsion contains 35 vol% water and the nonaqueous phase contains 1.9 wt% solids. Due to the high viscosity and opacity of the emulsion, microscopic examination of the emulsion was difficult, and thus an average droplet diameter could not be determined with any certainty. However, by adding one or two drops of a 50:50 by volume heptol solution to a small emulsion sample, droplets varying from 1 to 50 µm could be discerned. Fig. 4 shows the free water resolution with time (where time zero is the end of the first centrifugation) for the AEC emulsion, as received. The emulsion is relatively stable, with only 12% of the water resolved after 8 h of treatment. The unresolved water remained dispersed in the continuous phase.

Figs. 2b and 3 show a TEM image and a particle size distribution of the solids from the AEC emulsion, respectively. The particles appear to be irregular-shaped platelet struc-

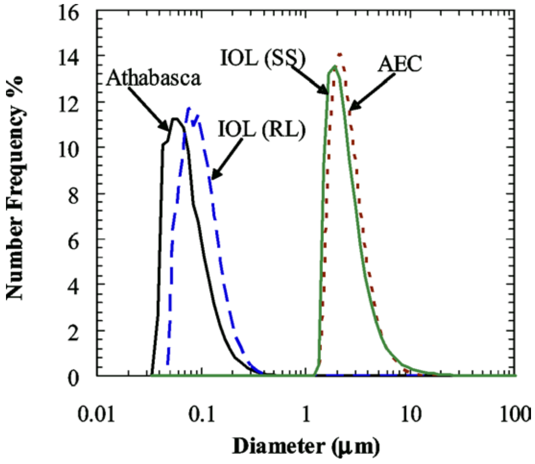

Fig. 3. Particle size distributions of Athabasca fine solids, AEC wellhead solids, IOL refinery rag-layer solids, and IOL refinery solids-slurry solids.

tures with diameters between 1 and 10 μm. An XRD analysis (not shown here) indicated that these solids are clays similar to the Athabasca solids. However, they are approximately 50 times greater in diameter, on average.

3.1.3. *Refinery emulsion*

The IOL refinery emulsion contains 43 vol% water and the nonaqueous phase contains 2.1 wt% solids. Microscopic examination of the emulsion as received indicated water droplets varying from less than 10 up to 350 μm with a Sauter mean diameter of 146 μm. This emulsion was very stable under normal gravity but, as shown in Fig. 4, it is quite unstable after heating and centrifugation. Approximately 80% of the water was resolved after 5 min of centrifugation and the emulsion was 90 to 95% resolved after 6 to 8 h of treatment.

As was mentioned previously, four distinct phases separated during this first centrifugation step: a continuous phase, a rag layer (RL), a free-water phase, and a solids slurry (SS). The rag layer accounted for 9 vol% of the total emulsion with a Sauter mean diameter of 30 μm. The solids slurry made up 7 vol% of the total emulsion with a Sauter mean diameter of only 8.1 μm. The continuous phase was free of water. As was shown in Table 3, the solids content of the continuous phase, the rag layer and solids slurry were 0.11, 1.8, and 11.8 wt%, respectively. The stability of the rag layer and solids slurry emulsions was also assessed as shown in Fig. 4. After 8 h of treatment, 85% of the water from the rag layer was resolved, while zero water was resolved from the solids slurry. It appears that the IOL emulsion consists of or separates into two distinct emulsions.

Figs. 2c and 2d are TEM micrographs of the solids separated from the IOL emulsion rag layer and solids slurry, respectively. Fig. 3 shows the particle size distributions of the same two solids samples. The rag layer solids are similar in size and shape to the fine solids from the Athabasca bitumen sample, while the solids slurry solids are similar to the coarse AEC wellhead sample solids.

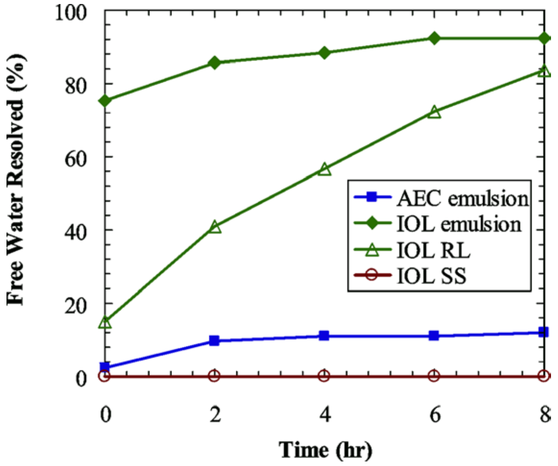

Fig. 4. Free-water resolution with time for AEC wellhead emulsion, IOL refinery emulsion, IOL refinery rag layer, and IOL refinery solids slurry. Time zero is the end of the first centrifugation.

3.1.4. *Summary*

There appear to be two classes of native solids that contribute to emulsion stability: (1) fine solids less than 500 nm in diameter; (2) coarse solids from 1 to 10 μm in diameter. They both have platelet structures and are predominantly clays. It is interesting to note that the IOL emulsion appears to contain two distinct sizes of solids. It is possible that this emulsion is a combination of two or more different emulsions (for example, emulsions similar to the oilsands and AEC emulsions), and that each contain a specific size class of solids. The role of each class of solid in stabilizing emulsions is considered separately below.

3.2. *The role of fine solids*

Since Athabasca and IOL fine solids appear to be similar in size and composition and there was a limited supply of the IOL fine solids, only Athabasca fine solids were used for these experiments. Figs. 1 and 5 show that emulsions stabilized by asphaltenes and Athabasca fine solids experience less free-water resolution than those stabilized by asphaltenes alone. Note that, while the difference in stability is modest under the imposed treatment, the enhanced stability can potentially be significant, for example, in a conventional heater-treater. Fig. 5 also shows that the emulsions prepared from the Athabasca Bitumen 2 asphaltenes are less stable than the emulsions prepared from Bitumen 1 asphaltenes. The average molar mass of Athabasca Bitumen 1 asphaltenes was previously measured in toluene using vapor pressure osmometry [52]. Although not shown here, the Bitumen 2 asphaltenes have a molar mass 30% smaller than that of the Bitumen 1 asphaltenes confirming that asphaltene properties have a significant impact on emulsion stability even for emulsions partially stabilized by solids.

For the data shown in Figs. 1 and 5, the solid concentration in the AS emulsions varies from approximately 0.05 to 1.7 kg/m^3. In order to assess interfacial composition, a

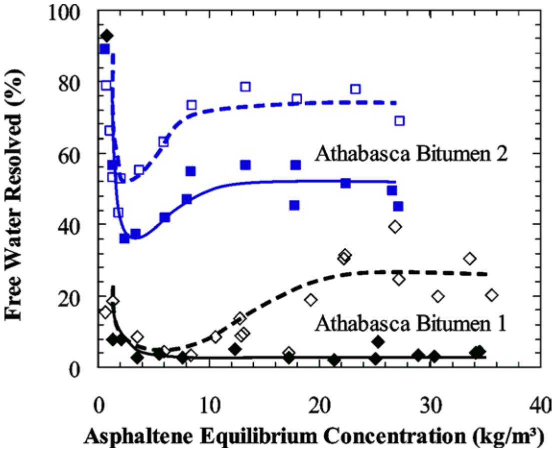

Fig. 5. Emulsion stability after 2 h for model emulsions stabilized by (a) Athabasca Bitumen 1 asphaltenes and asphaltene–solids, (b) Athabasca Bitumen 2 asphaltenes and asphaltene–solids (25/75 heptol, 40 vol% water). The closed symbols indicate AS and the open symbols indicate asphaltenes only. The lines are visual aids.

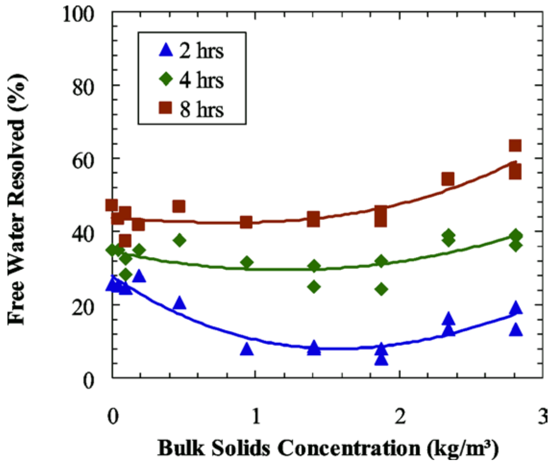

Fig. 6. Emulsion stability after 2, 4, and 8 h for Athabasca Bitumen 1 asphaltenes and fine solids (25/75 heptol, 40 vol% water, 1.9 kg/m^3 asphaltenes). The lines are visual aids.

new set of experiments was performed at a fixed asphaltene concentration of 1.9 kg/m^3 and solids concentrations in the range indicated by Fig. 6. Fig. 6 indicates that the enhanced stability is a function of the concentration of the solids. At a treatment time of 2 h, emulsion stability increases as the solids concentration increases up to approximately 1.5 kg/m^3. At all times, stability decreases at solids concentrations greater than 2 kg/m^3.

Fig. 7 shows that the solids fractional surface coverage on the interface increases with solids concentration [29]. It appears that the fine solids compete with the asphaltenes to adsorb on the interface. The most stable emulsions (least free water) occur when 60 to 80% of the area of the water/oil interface is covered by asphaltenes and 20 to 40% is covered by solids, that is, at approximately a 2:1 fractional area ratio of asphaltenes to solids. We speculate that there is a synergy between the asphaltenes and the solids; asphaltenes maintain a rigid interface while the solids form a barrier between the water droplets. At lower solids-to-asphaltene ratios, there are insufficient solids to form an effective barrier, while at higher ratios, insufficient asphaltenes remain on the interface to immobilize the solids on the interface.

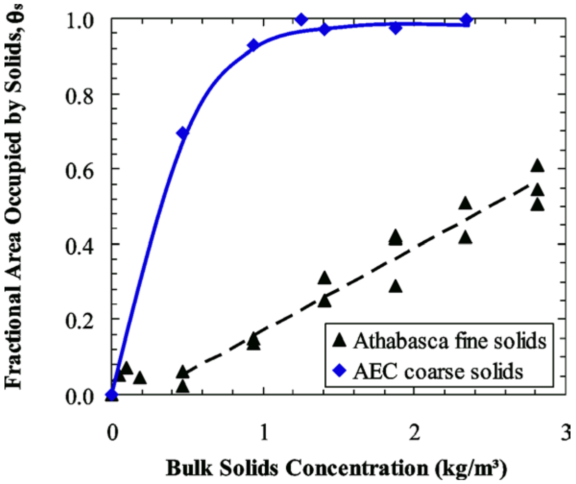

Fig. 7. Fractional area occupied by solids on water–oil interface for model emulsions stabilized by asphaltenes and (a) fine solids, (b) coarse solids (25/75 heptol, 40 vol% water, 1.9 kg/m^3 asphaltenes). The lines are visual aids. Fine solids data from Sztukowski and Yarranton [29].

3.3. The role of coarse solids

Since only a limited supply of IOL coarse solids was extracted from the solids slurry and the coarse IOL and AEC solids are similar in size and nature, only the AEC solids were considered for these experiments. Table 2 indicated that the solids content of the AEC emulsion was 1.9 wt% or an equivalent solids concentration of approximately 19 kg/m^3. Hence, to reproduce the original AEC emulsion stability, it was necessary to utilize a solids concentration ten times greater than that used for the fine solids emulsions discussed in the previous section.

Fig. 8 shows the stability of emulsions created from Athabasca Bitumen 2 asphaltenes at a concentration of 1.9 kg/m^3 and solids varying in concentration from 0 to 25 kg/m^3. When AEC solids are present in concentrations less than 5 kg/m^3, unstable emulsions will result with complete water resolution after 8 h for emulsions containing less than 1 kg/m^3 solids. However, as the solids concentration increases, the free water resolution decreases, a result consistent with the work of others [7,15,17,19,32,33,35]. For solids concentrations exceeding 10 kg/m^3, the free-water resolution of the model emulsion is approximately the same as that of the original AEC emulsion.

It is interesting to note that although the asphaltene concentrations for the model system (1.9 kg/m^3) and the actual emulsion (160 kg/m^3) are markedly different, the actual emulsion stability can be reproduced. This result suggests that at high enough concentrations, coarse solids alone are sufficient to impart long-term stability to an emulsion. This

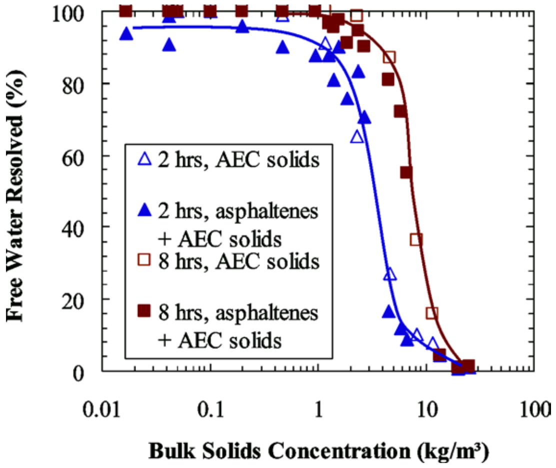

Fig. 8. Emulsion stability after 2 and 8 h for (a) Athabasca Bitumen 2 asphaltenes and AEC coarse solids and (b) AEC coarse solids. The lines are visual aids.

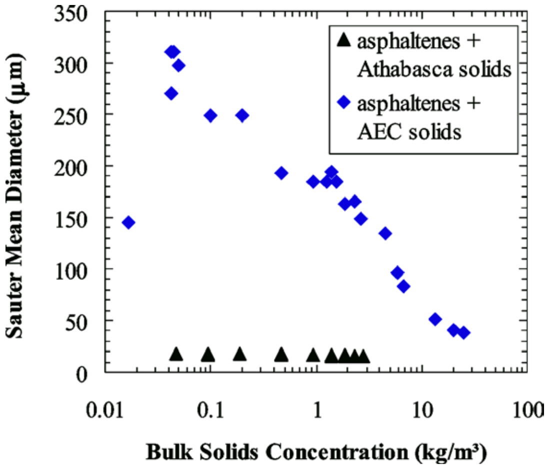

Fig. 9. Sauter mean diameter for (a) Athabasca Bitumen 1 asphaltenes and fine solids; (b) Athabasca Bitumen 2 asphaltenes and AEC coarse solids.

is confirmed by the additional results in Fig. 8, which show that emulsions consisting solely of AEC solids at bulk concentrations exceeding 5 kg/m^3 have the same free-water resolution as those containing both asphaltenes and solids.

Fig. 7 indicates that AEC solids replace all asphaltenes on the interface for bulk solids concentrations exceeding 1 kg/m^3. Although the interface appears to be predominantly occupied by asphaltenes at solids concentrations below 1 kg/m^3, the emulsions are very unstable and are completely broken after 8 h of treatment. Note that an emulsion stabilized by 1.9 kg/m^3 Athabasca Bitumen 2 asphaltenes with no solids had only 63% resolved water after 8 h of treatment. The high free-water resolution of these emulsions with low AEC solids concentrations is linked to the large average droplet size, as indicated in Fig. 9. The droplet diameters are 10 times larger than those encountered in asphaltene or asphaltene and fine solids stabilized emulsions for low bulk solids concentrations. These results suggest that there is significant coalescence of droplets during the settling period even though the interface is primarily occupied by asphaltenes. It is speculated that the few solids that do adsorb on the interface act as bridges between water droplets and facilitate coalescence. To test this hypothesis, AEC solids at a concentration of approximately 0.5 kg/m^3 were gently stirred into a settled emulsion stabilized solely by Athabasca Bitumen 2 asphaltenes. The Sauter mean diameter increased from 17 to approximately 180 µm within minutes. Hence, it appears that the AEC solids are capable of acting as bridges and facilitating coalescence at low concentrations.

When the solids concentration surpasses 1 kg/m^3 and continues to increase, particles can potentially either form a multilayer around the droplet or become trapped in the continuous phase between adjacent water drops. Trapped droplets or a thicker steric barrier prevent aggregation among water droplets and direct bridging of solids between interfaces, thus reducing coalescence and the overall free water resolution. Reduced coalescence is confirmed by the decrease in the Sauter mean diameter at higher bulk solids concentrations, as shown in Fig. 9. It appears that film rigidity imparted by asphaltenes adsorbed on the interface is unnecessary for achieving high emulsion stability if solids are present in high enough concentrations.

3.4. Treatment of emulsions stabilized by fine and coarse solids

Fig. 10 summarizes the hypothesized configurations of fine and coarse solids in the near interfacial region of an emulsion. The location of solids in an emulsion has consequences for emulsion treatment. If solids or asphaltenes are located on the interface, it is desirable to weaken the interface, for example, by introducing a chemical capable of replacing these particles with a material that will promote droplet coalescence. If, however, solids are not located on the interface but enhance an emulsion's stability by trapping or multilayer formation, a treatment based on particle flocculation would be more beneficial. If solids can be flocculated and concentrated in such a way that they do not hinder the aggregation of droplets, the interface of such an emulsion may be weak enough for coalescence. Two preliminary treatments based on these principles are considered here: toluene dilution and heptane dilution.

There is evidence that when the continuous phase is either strongly aromatic or strongly paraffinic, emulsions with low stability are created [8,50]. Hence, it is speculated that it may be possible to destabilize an existing emulsion if excess toluene (aromatic) or heptane (paraffinic) is added. In a good solvent such as toluene, asphaltenes are more mobile and form a weaker, less elastic interface. Excess toluene may further weaken the interface and promote droplet coalescence. In a poor solvent such as heptane, asphaltenes may precipitate and flocculate and be less likely to adsorb on and stabilize the interface. Heptane may also cause solids to flocculate and become less effective stabilizers. The effect of toluene and heptane dilution is discussed below for emul-

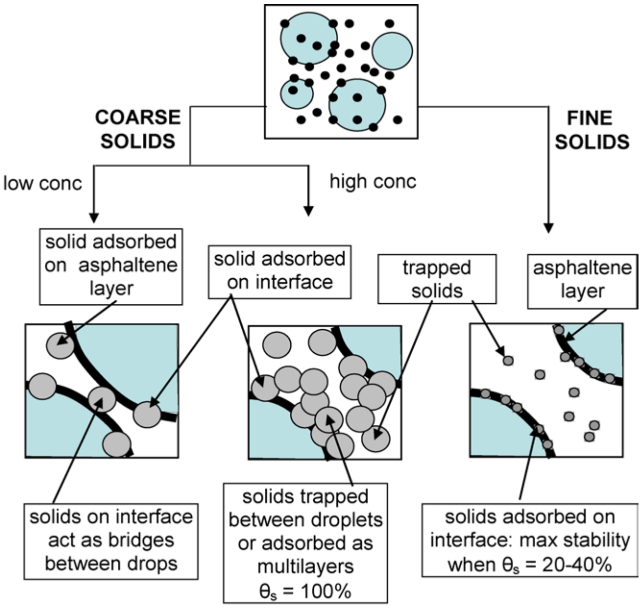

Fig. 10. Possible distributions of coarse and fine solids in an emulsion.

sions stabilized by asphaltenes, asphaltenes and fine solids, and asphaltenes and coarse solids.

3.4.1. *Effect of solvent dilution on asphaltene-stabilized emulsions*

Model emulsions were prepared from Athabasca Bitumen 2 asphaltenes at 5 kg/m^3 in 25/75 heptol and allowed to settle for 1.5 h. The continuous phase that evolved during the settling time was decanted until only concentrated emulsion remained. Toluene or heptane was then added to the concentrated emulsion at ratios varying from 0.2 to 2.8 cm^3/cm^3 solvent/emulsion, which corresponds to a solvent/continuous phase ratio of 0.6 to 7 cm^3/cm^3. The mixtures were shaken on a shaker table for approximately 2 min to ensure that the solvents were entirely dispersed throughout the emulsion. The mixtures were poured into centrifuge tubes, capped, and subjected to destabilization treatment as outlined in Section 2. Note that the free-water resolution for these experiments is reported after 2 h.

Fig. 11 shows that the addition of toluene increases the free-water resolution by 30% once the toluene/continuous phase ratio exceeds 1 cm^3/cm^3. The addition of toluene does appear to weaken the interface and promote coalescence. On the other hand, heptane dilution results in very stable emulsions with no free-water resolution for dilution ratios exceeding 1 cm^3/cm^3 heptane/continuous phase. Note that the heptane content of the continuous phase at the lowest and highest dilution ratios was 60 and 95%, respectively, which is above the onset of precipitation (at 45% heptane). At first glance, the increased stability contradicts previous work [8,50] indicating that if sufficient heptane to precipitate asphaltenes is added *prior* to emulsification, the emulsions are unstable. However, in this case, the heptane was added *after* emulsification. It appears that as the continuous phase becomes a poor solvent, the asphaltenes adsorbed on the interface become trapped on the interface and are not precipitated. They appear to form a stronger film that provides more resistance to coalescence.

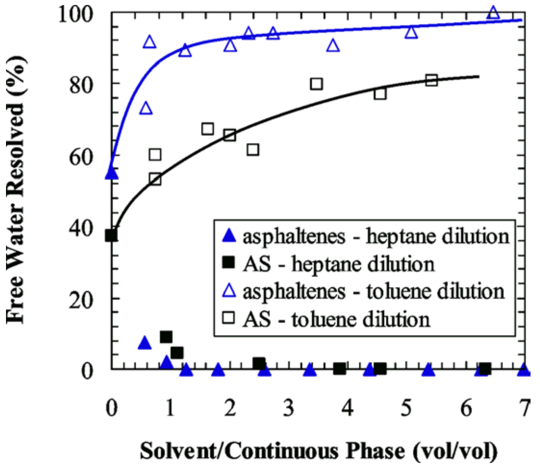

Fig. 11. Effect of solvent and solvent concentration on free-water resolution of Athabasca Bitumen 2 asphaltenes and AS stabilized emulsions after 2 h of treatment. The lines are visual aids.

3.4.2. *Treatment of emulsions with fine solids*

Model emulsions were prepared from Athabasca Bitumen 2 asphaltene–solids at a total concentration of 5 kg/m^3 in 25/75 heptol. As noted in Table 1, the solids made up 3.1 wt% of the asphaltene–solids and hence the solids concentration was 0.15 kg/m^3. The emulsions were settled for 1.5 h and the continuous phase was decanted. The concentrated emulsions were diluted at ratios similar to those used for the asphaltene-stabilized emulsions. The free-water resolution was again reported after 2 h.

Fig. 11 shows that the addition of toluene results in an additional 30% free water when the dilution ratio exceeds 2 cm^3/cm^3 toluene:continuous phase. Heptane dilution results in very stable emulsions with no free-water resolution for heptane ratios greater than 1 cm^3/cm^3. While the presence of solids increases emulsion stability in general, it appears that the effect of the diluent on the asphaltenes is the dominant factor in the treatment. Toluene addition weakens the interface and results in more coalescence. Heptane addition strengthens the interface and results in less coalescence than no treatment at all.

As a comparison, the IOL rag layer was also treated with a 1:1 volume ratio of solvent to emulsion dilutions (2 cm^3/cm^3 solvent:continuous phase). The rag layer was stabilized by asphaltenes and fine solids with a solids concentration of 33 kg/m^3. The toluene and heptane treatments achieved 84% and 29% free-water resolution, respectively. The results are consistent with those for the model emulsions prepared from Athabasca asphaltene–solids. Hence, even at relatively high fine solids concentrations, the effect of the solvent on the asphaltenes appears to be the dominant factor in the treatments.

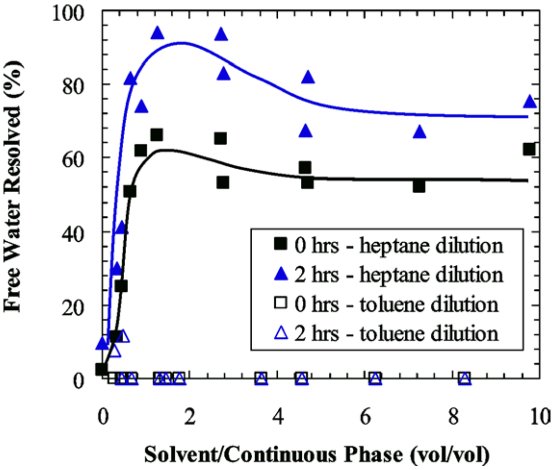

Fig. 12. Effect of solvent and solvent concentration on free-water resolution of AEC emulsion. The lines are visual aids.

3.4.3. *Treatment of emulsions with coarse solids*

Fig. 12 shows the effect of toluene and heptane dilution on the AEC emulsion. Toluene addition did not destabilize the emulsion, even at high dilution ratios and after 8 h of treatment. However, heptane addition significantly destabilized the emulsion, even at dilution ratios below the onset of asphaltene precipitation at a dilution ratio of 1.3 wt/wt heptane:bitumen (2.0 $\mathrm{cm^3/cm^3}$ heptane:continuous phase). In fact, the maximum free-water resolution is experienced just below the onset of precipitation.

Recall that coarse solids at high concentrations appeared to stabilize the emulsion by preventing contact between droplets. They also dominated the interface so that asphaltenes are not expected to play a significant role in stabilizing the emulsion. We speculate that heptane addition causes the solids to flocculate. Flocculated solids are far less likely to form a continuous barrier between the water droplets, and hence, coalescence can occur. A brief test in which heptane was added to wet AEC solids indicated that they flocculated into aggregates varying from 20 to approximately 200 μm in size, as indicated by the micrograph in Fig. 13a. The flocculation of these solids in heptane confirms that they have some adsorbed hydrocarbon matter. Fig. 13b shows that the solids did not flocculate in toluene. The toluene treatment is therefore ineffective because the primary stabilization mechanism remains in place. Note that with sufficient dilution and agitation, any solvent could likely break this emulsion simply by reducing the concentration of the solids (see Fig. 8). However, flocculation of the solids clearly promotes emulsion breaking.

With the heptane treatment, the maximum free-water resolution occurred at the onset of asphaltene precipitation. It is possible that precipitated asphaltene particles simply add to the total concentration of particles, increasing the stability of this solids-stabilized emulsion. It is also possible that as heptane is added some asphaltenes are driven to the interface and that at high heptane dilutions they enhance emulsion stability. In either case, the maximum in free water would occur at the onset of precipitation.

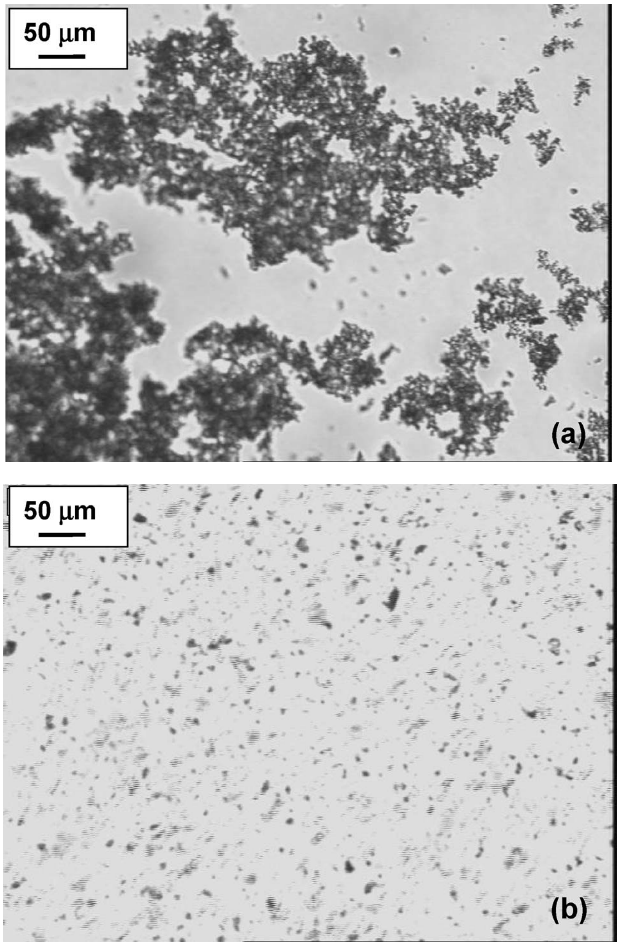

Fig. 13. Micrographs of AEC solids dispersed in (a) pure heptane, (b) pure toluene.

The IOL solids slurry was also treated with a 1:1 volume ratio of solvent to emulsion dilutions (2 $\mathrm{cm^3/cm^3}$ solvent:continuous phase). The toluene and heptane treatments achieved 13% and 23% free-water resolution, respectively. The toluene treatment results are consistent with those for the AEC emulsion. Although the heptane treatment outperformed the toluene treatment, it was less effective than the heptane treatment of the AEC emulsion. It is possible that additives present in the IOL solids slurry reduce the effectiveness of the heptane treatment.

4. Conclusions

Fine solids, i.e., platelet-shaped particles ranging from 50 to 500 nm, compete with asphaltenes to adsorb on the interface. These solids adsorb flat on the interface and likely form a partial barrier to water bridging between droplets. A combination of asphaltenes and fine solids at the water/oil interface in a 2:1 fractional area ratio creates a maximum in emulsion stability. If there are too few solids, there is insufficient surface coverage to provide extra stability, whereas too many solids results in an interface that is not rigid enough to maintain stability.

Relatively low concentrations of coarse clays destabilize emulsions because they replace asphaltenes on the interface and cannot stabilize small water droplets. Coarse solids may also act as bridges between individual water droplets, increasing the mean diameter of water droplets and the overall coalescence. Conversely, relatively high concentrations of coarse clays strongly stabilize emulsions because they prevent close contact between water droplets or form multilayers on the interface.

The most effective treatments for emulsions stabilized by fine clays appear to be those that weaken the interfacial film or replace the solids and asphaltenes on the interface with a poorer stabilizer. Emulsions stabilized by coarse particles are most effectively broken when solids are flocculated so that they can no longer prevent close contact between water droplets. Refinery emulsions containing both types of solids may require more than one type of treatment, or even process step, for effective water resolution.

Acknowledgments

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Appendix A. Nomenclature

C_A^{eq}	asphaltene equilibrium concentration (kg/m^3)
C_A^0	initial asphaltene concentration (kg/m^3)
d_{32}	Sauter mean diameter (m)
m_A	total mass of asphaltenes in emulsion (kg)
V_w	total volume of water phase (m^3)

Greek symbols

Γ_A	asphaltene mass surface coverage (kg/m^2)
Γ_A^m	asphaltene monolayer mass surface coverage (kg/m^2)
θ_A	fractional area occupied by asphaltenes on interface (–)
θ_S	fractional area occupied by solids on interface (–)

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