

Factors Contributing to Petroleum Foaming. 2. Synthetic Crude Oil Systems

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The influence of petroleum asphaltene and resins on stabilizing model oil foams comprised of light mineral oil mixed with toluene (minerol) was investigated. Two factors contribute significantly to foam volume and stability: bulk viscosity and asphaltene state of aggregation. An increase in bulk viscosity was found to increase foam stability as gauged by the total time required for a foam to collapse. Asphaltene aggregation is governed primarily by the solvent aromaticity and resin/asphaltene (*R/A*) ratio. There is a threshold size in the state of asphaltene aggregation above which the ability of these aggregates to stabilize foams is markedly reduced. This appears to be closely related to asphaltene flocculation and precipitation at compositions beyond the solubility limit of the asphaltenes. Solvent systems generating the highest foam volume were found to reduce the air-oil surface tension to the greatest extent. Addition of an asphaltene dispersant increased the foamability of asphaltenes in minerol and seems to indicate that asphaltenes enhance foam stability when they are well dispersed or dissolved and in solvent mixtures in which they are highly surface active. By analogy to the role of asphaltenes in stabilizing emulsions, the highest foam stability was observed for asphaltenes near their solubility limit, the thermodynamic state at which asphaltenic aggregates are most surface-active. Addition of resins, similar to addition of dispersants, increased foam stability, presumably by decreasing the size of asphaltene aggregates.

1. Introduction

The stability and breaking of nonaqueous foams is a subject of great importance to the petroleum industry. Nonaqueous foams occur in the production of and refining of crude oil. Crude oil foams can pose major problems for operators of gas/oil separation plants, causing a loss of crude in the separated gas stream and consequent loss of revenue and possible damage to downstream compressors. Foaming of crudes is particularly troublesome during decompression and handling on offshore platforms, where the rate of processing is high and the space available is limited. Despite the importance of this topic, much of the available literature on foam stability and destabilization makes no clear distinction between aqueous and nonaqueous systems.

A number of researchers^{1–8} have worked specifically with nonaqueous systems and highlighted certain factors as being important in nonaqueous foam stability, i.e., bulk viscosity, interfacial viscosity, and surface

tension. Brady and Ross¹ in studying a series of engine and medicinal grade paraffin oils found that foam stability increased linearly with kinematic viscosity of the oil. This correlation of stability with viscosity was confirmed by McBain and Robinson,² both in the bulk and surface. They attributed the high surface viscosities they had observed to the formation of plastic films at the gas/liquid interface. More labile films comprised of highly surface-active amphiphilic molecules appear to enhance foam stability appreciably. Surface tension⁶ has been shown to play a role in nonaqueous foam stability, but does not appear to be as dominant as the preceding factors.^{2,7} The presence of surface-active materials has often been presumed necessary for foaming to occur in nonaqueous media.^{3,8,9} Sirota and co-workers¹⁰ have recently demonstrated that surface crystallization of *n*-alkanes can confer appreciable stability on foam bubbles. They showed that the microscopically observable foam stability is related to crystallization of a microscopic monomolecular layer at the liquid–vapor interface at a temperature above the bulk melting temperature. McBain et al.³ indicated that treating aviation lubricating oils with activated charcoal de-

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creased the foamability of this oil. They assumed that activated charcoal removed the polar compounds present in the lubricating oil that cause it to foam. However, they did not specify the chemical composition of these compounds, other than being soluble in benzene and pyridine. For crude oils, the presence of specific acids and phenols has been shown to be important for foam formation and stability.¹¹

The heaviest fraction of crude oil is termed asphaltene, which is heptane insoluble and toluene soluble. Asphaltenes are polynuclear fused aromatic sheets with different polar functional group substituents and alkyl chains on the periphery of the aromatic core. Owing to their relatively high polarity, asphaltenes are known to adsorb at the oil/water interface and stabilize water-in-crude oil emulsions. Many researchers have published on the role of asphaltenes in stabilizing water-in-oil emulsions.^{12–21} However, to date, their role in stabilizing crude oil foams was briefly mentioned by Cassani et al.²² In addition to asphaltenes, another surface-active fraction of crude oils termed resins exists; this fraction has lower polarity and lower molecular weight compared to asphaltenes.²³ Resins are believed to adsorb onto the asphaltene aggregates and act as a solvating agent.^{24–26}

A proposed aggregate structure of asphaltenes was first suggested by Pfeiffer and Saal²³ in which asphaltenes form a polynuclear aromatic dense core, solvated by resins. On the basis of this hypothetical picture, resins act to solvate the asphaltene core. In fact, asphaltenes can form aggregates without being solvated by resins, at least in many organic solvents.²⁷ The pronounced tendency of asphaltenes to form aggregates in hydrocarbon solution is one of their most characteristic traits. Thus, while a number of experimental methods indicate that isolated asphaltene “monomers” have an average molecular weight of the order of 1,000

g/mol, numerous methods including VPO, SEC, and scattering techniques (SAXS, SANS) show that they associate spontaneously in most hydrocarbon media, arriving at empirical molecular weights of several thousand daltons or more (VPO) and with physical dimensions from 2 to 15 nm (SAXS, SANS). These aggregates are commonly referred to as micelles in the literature, based on an analogy drawn early on^{28–31} with the behavior of surfactant molecules in solution. Properly speaking, these aggregates are not micelles, because they are not topologically ordered with an “inside” and an “outside”, a defining feature of micelles. In fact, they resemble closely the type of noncooperative aggregation observed in dye molecule stacking, largely driven by π -bond overlap and dipolar or H-bond interactions between polar functional groups in the nonaqueous solution. In the case of asphaltenes, the aggregation is likely terminated due to steric packing constraints with aggregates much larger than 4–5 monomers, due to the aliphatic side chains on the asphaltene monomers. Under unfavorable solvent conditions (i.e. when the solvent becomes increasingly aliphatic), the asphaltene micelles are prone to further aggregation into clusters that are unstable and precipitate. The generally accepted picture of the physical behavior of asphaltenes in hydrocarbon media is illustrated schematically below:³²

asphaltene molecules \Rightarrow aggregates \Rightarrow
aggregate clusters/flocs

The asphaltenes appear to display the same solubility behavior both in crude petroleum and in simpler organic solvents.^{33,34} Studies on asphaltenes dissolved in hydrocarbon solvents have shown that the dimensions of the aggregates depend strongly on the nature of the solvent, the asphaltene concentration, and the temperature.

Asphaltene aggregates formed in hydrocarbon media fall into the colloidal regime.^{27–30,34} Considerable effort has been dedicated to understanding the physical nature of the interaction of the asphaltene colloids with the hydrocarbon medium and, in particular, the basis for their stability in crude oil under reservoir conditions. Empirical observations indicate that the resins play an important role in stabilizing asphaltenes in crude oil.^{27,35} The resins differ from asphaltenes in having a higher solubility in the petroleum medium: they are soluble in heptane. VPO and scattering studies^{36,37} on isolated resin fractions show that they too tend to self-associate in organic solvents. Resin and asphaltene fractions are probably best viewed as two “adjacent” portions of a single broad compositional continuum that contains the more polar, aromatic, and higher molecular weight components of petroleum.

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In Part I of this series,³⁸ we have studied the foamability of twenty crude oils in an attempt to correlate foaminess with different crude oil components. We have found that foam collapse slope correlates with asphaltene content in asphaltenic crudes, while foaminess (foam height) correlates with surface tension in crudes having small amounts or no asphaltenes. Owing to the great complexity and diversity of crude oil chemistries, it was not possible to discern the effect of individual crude oil components on crude oil foamability. In the current work, we investigate the specific influence of petroleum asphaltenes and resins on crude oil foaming. Asphaltenes and resins were isolated from crude oils and dissolved in solvent mixtures of varying aromaticities. In previous studies, McLean and Kilpatrick used *n*-heptane and toluene (heptol) mixtures to model the solvency of the crude oil system.^{39,40} Due to the low viscosity of heptol mixtures, it was not possible to generate stable foams in model heptol solutions. Consequently, *n*-heptane was replaced by a more viscous material (light mineral oil), which has a comparably aliphatic chemical structure. These mineral oil–toluene mixtures are termed mineral solutions. Mineral oil viscosity is 28.4 cP at 40 °C, and it is composed of a mixture of paraffinic hydrocarbons ranging from C₁₅ to C₄₁ with C₂₁ as the major component of this mixture (34.08 wt %).

2. Experimental Section

2.1. Materials. HPLC grade solvents (toluene, *n*-heptane and dichloromethane) were used. Light mineral oil was a high-purity grade (dynamic viscosity at 25 °C was 69.92 cP, and specific gravity at 25 °C was 0.849 g/mL). All chemicals were supplied from Fisher Scientific. Asphaltenes were precipitated from Arab Heavy (sometimes known as Safaniya) crude oil and resins were isolated from both Arab Heavy and Africa crudes. Ultrahigh Purity nitrogen gas (99.999% purity) containing 1 ppm water was used to generate foams.

2.2. Methods. *2.2.1. Asphaltene and Resin Isolation.* Briefly, the asphaltenes were precipitated from the crude oil (Arab Heavy or Africa) in an excess of *n*-heptane at room temperature, then the resins were isolated after adsorption of the heptane-soluble portion on activated silica gel by sequential elution column chromatography. A detailed description of these methods is published.⁴¹

2.2.2. Model Oil Preparation. The requisite mass of Arab Heavy (AH) asphaltenes was weighed to the nearest 0.1 mg accuracy in a Teflon capped glass vial. Toluene was added to asphaltenes, shaken for 1 h, whereupon mineral oil was added. The mixture was shaken again for 1 h. Resins (Africa or AH) were weighed to the nearest 0.1 mg accuracy in a Teflon capped glass vial. Toluene and mineral oil mixture was added to resins and shaken for 1 h. When asphaltenes and resins were employed together, first asphaltenes were weighed, and the necessary volume of toluene was added. The solution was shaken for 1 h, added to a weighed resins and mineral oil mixture, and shaken for another hour.

2.2.3. Foam Generation Procedure. Solutions were foamed in a smaller version of the sparge apparatus described in the Experimental Section of Part I. A fritted sparge tube of pore

size 10–20 μm from Ace Glass was used. Nitrogen gas was purged through a column packed with anhydrous calcium sulfate 8 mesh size (Drierite). The dried nitrogen gas passed through a 0.45 μm filter. A 15 mL sample of the model oil was placed in the liquid reservoir and nitrogen gas was bubbled at a rate of 250 mL/min. The foam volume was recorded from the beginning of the gas flow at 15 s intervals for the first minute and then at 30 s intervals for the next 9 min. The maximum foam volume after the 10 min period is recorded as the foam volume. The collapse time was measured from the time the gas flow was stopped until two or three bubbles remained, following Ottewill and co-workers.⁴²

2.2.4. Dynamic Shear Viscosity. Viscosities were measured with a Dynamic Stress Rheometer (Rheometrics). A 20 mL sample of the model oil is placed in a double couette geometry at 25 °C, and a steady stress sweep was applied ranging from 0.01 to 100 Pa. The viscosity reported in Pa-s was taken as that portion of the viscosity-stress regime in which the viscosity was essentially stress independent. This was typically in the range 40–700 mPa.

2.2.5. Surface Tension and Density. Surface tensions were measured with a Fisher autotensiomat (model 215), having a sensitivity of 0.02 dynes/cm and a relative accuracy of ± 2%. The apparatus employs the du Nouy ring method, and the sample was placed in a double-jacketed glass cell connected to a thermostated water bath adjusted at 25 °C. The densities of these solutions were measured with a 2 mL Moore-Van Slyke pycnometer (Fisher).

2.2.6. FTIR. FTIR spectra were obtained on a Nicolet Magna 750 Spectrometer. Samples were dissolved in HPLC grade CH₂Cl₂ as 10 g/L solutions. Spectra were obtained using a 0.2 mm fixed-path-length CaF₂ cell. The background spectrum of pure CH₂Cl₂ was obtained and subtracted from the sample spectra. Sixty-four scans were taken of each sample recorded from 4000 cm⁻¹ to 800 cm⁻¹ at a resolution of 2 cm⁻¹ in the transmission mode.

3. Results and Discussion

3.1. Effect of Asphaltene Concentration and Bulk Viscosity. Claridge and Prats⁴³ proposed a model and mechanism for anomalous foamy heavy oil behavior. They explained that the abnormally low viscosity associated with a foaming crude oil may be due to migration and adsorption of asphaltenes and resins to gas bubble surfaces and the formation of a semirigid coating. This coating prevents further bubble growth and coalescence. They assumed that as a result of asphaltene and resin migration from the bulk of the crude oil to the interface of the bubbles, the crude oil is depleted of this heavy fraction, resulting in a substantial viscosity reduction. To explore the relevance of the Claridge and Prats model to our foam system, we studied carefully the variation of asphaltene solvent conditions and its consequence on asphaltene surface activity.

The effect of asphaltenes on the foaming ability (defined as the foam volume recorded after 10 min at a specific gas flow rate) and foam stability (defined as the time taken from the instant after the gas flow was stopped to the last two or three bubbles) of model oils has been thoroughly investigated. The drainage of liquid from a single foam film can be related to that of liquid between parallel plates. Using this analogy, it can

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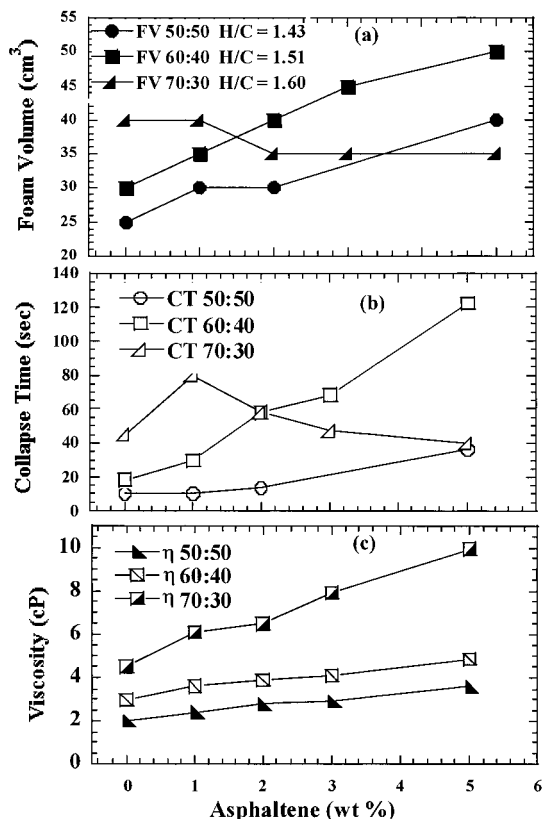


Figure 1. Dependence of (a) foam volume, (b) collapse time, and (c) bulk oleic solution viscosity on concentration of asphaltenes in solutions of mineral oil and toluene (minerol).

readily be seen that the approach toward a critical film thickness will be governed by the bulk viscosity of the foaming liquid. Obviously, highly viscous liquids will take longer to drain down to a given thickness than less viscous liquids, thus giving rise to longer-lived foams. It is therefore not surprising that for stabilized crude oil foams, it has been found⁴⁴ that the average foam lifetime L_f is linearly related to the crude oil bulk viscosity in the following manner:

$$L_f = a\eta_B + b$$

where L_f = the average foam lifetime in seconds, η_B = the bulk viscosity of the crude oil in mPa s, and a , b are the constants characteristic of the filler gas used to create the foam.

Figure 1 shows the dependence of foam volume, collapse time, and viscosity on asphaltene concentration in 50:50, 60:40, and 70:30 (v/v) mineral oil–toluene (minerol). It is clear from this figure that with both the 50:50 and 60:40 mineral systems, the foam volume, collapse time, and viscosity all increase monotonically as the concentration of asphaltenes in mineral is increased. However, with the 70:30 mineral case the foam volume and collapse time increase initially and then decrease as the asphaltene content is increased. Conversely, the viscosity in the 70:30 mineral case increases as asphaltene content is increased. Clearly, this implies that while increasing the model oil bulk viscosity through both asphaltene addition and increasing oleic solvent molecular weight is important in stabilizing foams, it is not the only relevant factor.

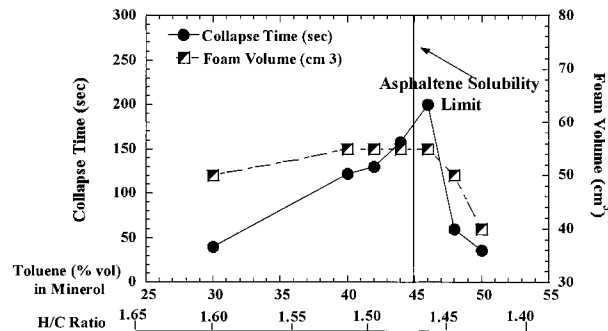


Figure 2. Dependence of foam volume and collapse time on toluene volume fraction in mineral (and corresponding solvent H/C ratio) in 5% AH asphaltene (w/w) solutions in mineral.

3.2. Effect of the Model Oil Solvency (H/C Ratio).

From Figure 1, it is seen that the incremental increase in foam volume and collapse time is greater with the 60:40 than with the 50:50 mineral system. This can be attributed to the fact that decreasing the toluene content of the solvent decreases asphaltene solubility, increases asphaltene state of aggregation, and may enhance asphaltene adsorption at the air–oil interface. The increased asphaltene concentration at the air–liquid interface would contribute to the foam stability by decreasing the rate of film drainage surrounding the foam. As mentioned by Ivanov et al.⁹ in their study of the factors affecting film thinning, an adsorbed surfactant layer (asphaltenes in our case) causes a slower fluid flow rate due to the appearance of a positive disjoining pressure at very small film thickness. However, with the 70:30 mineral system, an initial increase or plateau in the foam volume and collapse time is observed with increasing asphaltene concentration, followed by a subsequent decrease beyond 1% asphaltene. This is probably due to an increase in asphaltene aggregate size above an optimum, leading to flocculation and precipitation. The increased asphaltene aggregate size is accompanied by a rapid drainage of the asphaltenes from the air–oil interface due to their increased density or reduced surface activity.

The effect of the solvent H/C ratio was studied by varying mineral oil: toluene proportions (aromaticity is decreased with increasing mineral oil content and H/C ratio). Solutions of 5 wt % asphaltene concentration were prepared in mixtures of 50–70% mineral oil (i.e. 50–30% toluene) and were foamed to measure foam volume and collapse time (Figure 2). Clearly there is a maximum at a mineral H/C ratio of 1.46 (46% toluene in mineral) at which the highest foam stability (longest collapse time) is attained. It is also observed that the foam volume plateaus (55 cm³) in the range of 40–46% toluene. Through a filtration method, the asphaltene solubility limit in toluene–mineral oil mixtures was determined to be approximately 45% toluene. It should be noted that the solubility limit of AH asphaltenes in mineral solutions (45% toluene) is roughly 10% higher in toluene concentration than the corresponding limit in heptane–toluene solutions (40% toluene). It is interesting that this shift is consistent with the reduced solubility of asphaltenes with increasing alkane carbon number (Cimino et al.⁴⁵ and Hotier and Robin⁴⁶). It is clear from Figure 2 that the longest collapse time occurs at 46% toluene in mineral, very close to the asphaltene

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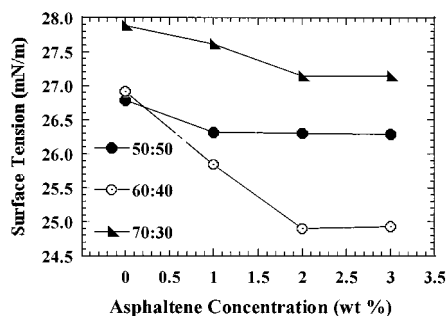


Figure 3. Surface tension–AH asphaltene concentration plots in solutions of varying toluene-mineral oil proportions.

solubility limit. These results suggest that asphaltenes stabilize foams and emulsions in similar fashions and maximum stability is attained when asphaltenes are at or near the point of precipitation. This reinforces the notion that the state of asphaltene aggregation and their corresponding surface activity are the decisive factors influencing foam generation and foam stability.

Sirota et al.¹⁰ studied the microscopic surface crystallization of *n*-alkanes at air–oil interfaces and its consequent effect on foam stability. They performed quantitative measurements on the lifetime and coalescence of bubbles impinging at the liquid–vapor interface, and showed that this foam stability is related to the recently reported crystallization of a microscopic monomolecular layer at the liquid–vapor interface at temperatures above the bulk melting temperature.^{47–51} This can help to explain why asphaltene-free mineral solutions exhibit finite foam stability.

3.3. Effect of Surface Tension. The surface tension of asphaltene–mineral oil–toluene solutions as a function of increasing asphaltene concentration was determined (Figure 3). The surface tension of the pure mineral mixtures increases as the mineral oil component is increased. The surface tension of the 50:50 mineral mixture was lowered modestly by the addition of 1 wt % asphaltenes, and it remained constant with further increase in asphaltene concentration. This small effect on surface tension is likely attributable to the high solubility of asphaltenes in this aromatic-rich solvent. The asphaltene molecules remain strongly solvated in the bulk adsorb weakly at the air–oil interface; with the 60:40 mineral mixture, the surface tension decreases substantially as the asphaltene concentration increases to 2 wt %. In our original experiments with these solutions (60:40 mineral), it was noted that beyond 2 wt %, asphaltenes formed small particulates which adhered to the DuNuoy ring. Clearly the presence of particulates and the trend of collapse time in Figure 2 indicate that, at this solvent condition, we have exceeded the solubility limit. Thus, surface tension values

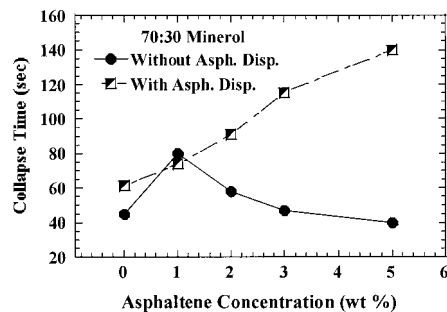


Figure 4. Comparison of foam stability in the presence and in absence of 1 wt % asphaltene dispersant. Base case is 70:30 mineral oil:toluene (v/v).

measured without filtering gave erroneously high surface tensions at this solvent condition. Therefore, the datum at 3 wt % asphaltenes and 60:40 mineral was obtained after filtering the solution. With the 70:30 mineral mixture, the degree of surface tension reduction is much lower than with the 60:40 mineral system. This is apparently due to gross precipitation of asphaltenes which produces even larger particles and which are not sufficiently surface active to either adsorb to the ring nor to the interface. In the 60:40 case, asphaltene aggregates are very surface active and adsorb strongly, exhibiting the greatest surface tension reduction. It is significant that this condition also corresponds to the greatest foam stability as evidenced by collapse time (of the three solvent conditions studied here). It is noteworthy that asphaltenes are not generally considered highly surface-active species. Asphaltene aggregation is not driven by amphiphilic properties but rather by π and H bonding in nonpolar media. The competition between self-association and surface adsorption appears to lead to maximum lability and surface activity near the solubility limit.

3.4. Effect of Adding an Asphaltene Dispersant. To further elucidate the effect of asphaltene aggregate size on foam generation and foam stability, experiments were performed with and without an asphaltene dispersant. The asphaltene dispersant utilized here was supplied by Nalco-Exxon Energy Chemicals, L. P. (product VX-6594). Such materials are used to prevent asphaltene deposition by dispersing and solvating them in crude oils. The dependence of foam collapse time on asphaltene concentration in 70:30 mineral with and without 1 wt % asphaltene dispersant is shown in Figure 4. Beyond 1 wt % asphaltene, added asphaltene dispersant clearly increases the foam collapse time. The dispersant apparently functioned well in decreasing the degree of flocculation and precipitation in this system, beyond 1 wt % asphaltene. The dispersant solvates the asphaltenes and maintains them in solution, while their surface activity remains high, much like the 60:40 solvent system.

3.5. Effect of Resin Concentration and Bulk Viscosity on Foam Properties. Resins are an important fraction of crude oil, representing as much as 22 wt % of crude oils.^{52,53} Two types of resins were studied: Arab Heavy (AH) and an especially acidic resin fraction termed Africa (AF) resins. Figure 5 provides

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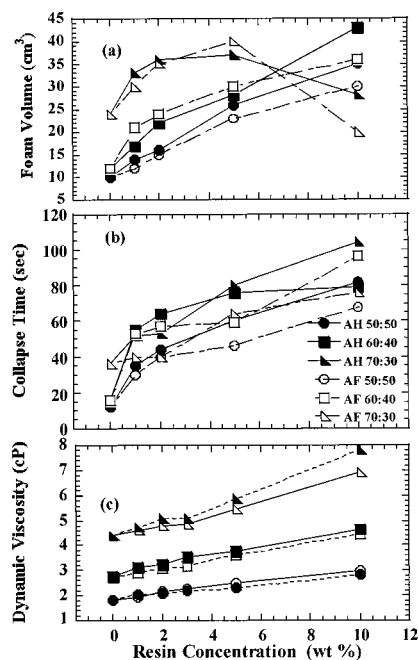


Figure 5. Dependence of (a) foam volume, (b) collapse time, and bulk oleic solution viscosity on concentration of AH and AF resins in solutions of varying mineral oil and toluene.

foam volume, collapse time, and viscosity as functions of resin concentration at varying solvent conditions (50:50, 60:40, and 70:30 mineral). It is clear that foam volume, collapse time, and viscosity all increase monotonically with the increase in resin concentration, with the exception of the decrease in foam volume at 5–10 wt % resins in 70:30 mineral. This decrease in foam volume for the 5–10 wt % resin at 70:30 mineral can be attributed to the increase in viscosity of the model oil. With the experimental foam configuration and the specified gas flow rate (250 mL/min), we observe that when the solution viscosity exceeds approximately 5–5.5 cP, the foam volume passes through a maximum and begins to decrease with increasing viscosity. In contrast, for the same conditions, it is observed that the foam collapse time continues to increase over the entire range of resin concentrations. It is thus seen that, irrespective of the type of solute and adsorbing species (i.e., resins or asphaltenes), foam volume achieves a maximum value at a specific bulk viscosity, which is a function of the details of the experimental setup (gas flow rate, sparge tube porosity, and cell diameter). Collapse time, however, more sensitively reflects the type of adsorbing species and their microstructure. With asphaltenes, the solubility limit is exceeded as mineral oil content increases from 50 to 60%. This manifests itself as local maxima in both collapse time (Figure 2) and surface tension reduction (Figure 3). We now examine the role of polar functionality in surface tension reduction and collapse time with resins.

3.6. Effect of Resin Chemical Structure on Surface Tension. Figure 6 provides low-field FTIR spectra for Africa and AH resins. The carbonyl and carboxylic acid stretches at 1700 and 1740 cm^{-1} are strong in the AF resin spectrum and virtually absent with AH resins. Clearly, the AF resins are highly polar and acidic, in comparison with the AH resins. The surface tension-concentration plots of these resins in varying mineral

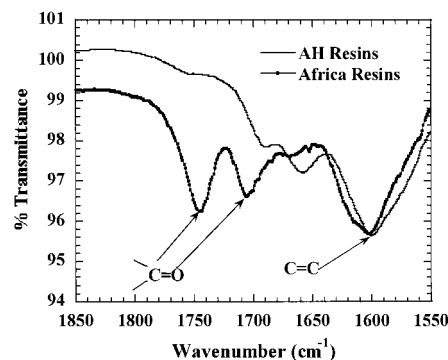


Figure 6. Low field (1550–1850 cm^{-1}) FTIR spectra of AH and AF resins in methylene chloride illustrating marked differences in carbonyl and acid contents.

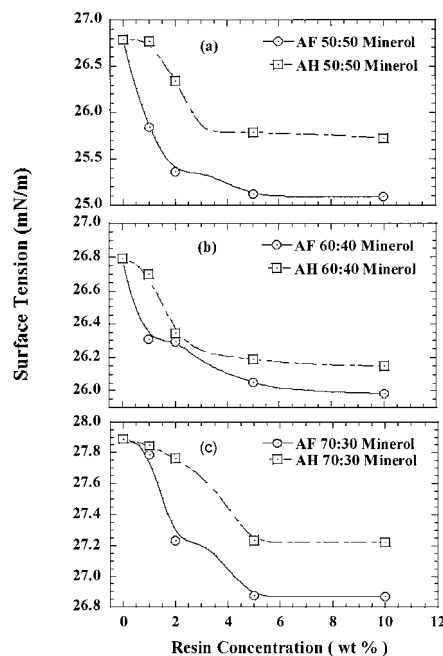


Figure 7. Surface tension as a function of AH and AF resin concentration in solutions of varying toluene–mineral oil proportions.

oil–toluene solvent systems at 25 °C are shown in Figure 7. Again, it is clear that AF resins are more surface active than AH resins. With respect to their foam properties (Figure 5), the foam volumes for both AF and AH resins are similar, while collapse times are somewhat higher at all solvent conditions with AH as compared to AF resins. It is perhaps surprising that despite the fact that AF resins are clearly more polar and surface active than their AH counterparts, there is little difference in collapse time of the respective foams with the AH-resin-stabilized foam being somewhat longer lived on the whole. This may be due to a somewhat higher viscosity of AH resin–mineral solutions, perhaps due to a higher molecular weight or greater degree of aggregation, evidence for which we have not specifically explored. It thus appears that with resins, bulk viscosity plays a central role in determining both foam volume and collapse time.

3.7. Comparison of Effects of Asphaltene Versus Resin Solution Viscosity on Foam Properties. Parts a and b of Figure 8 collect foam volume and collapse time data of both AH asphaltene–mineral and AH resin–mineral solutions as a function of bulk

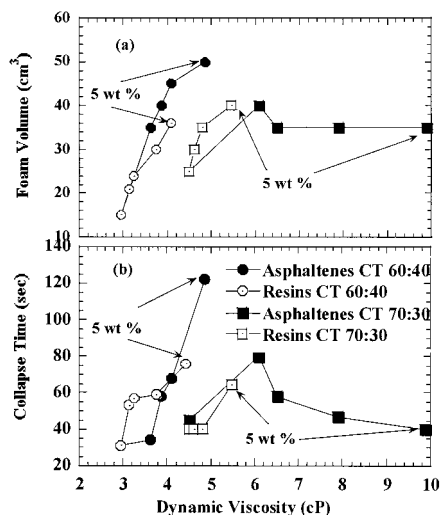


Figure 8. Foam volume (a) and collapse time (b) of AH asphaltenes and resins correlated to bulk oil viscosity.

solution viscosity. Noteworthy is the remarkably similar trending of the data. It is clear that the viscosity of asphaltene solutions are higher than that of resin solutions at the same concentration, this is attributed to the higher molecular weight of asphaltenes as compared to resins. Furthermore, asphaltenes tend to associate with the increase of the volume percent of mineral oil in mineral solvent mixture, while resins do not exhibit the same phenomenon. Asphaltene aggregation results in increased viscosity of the solution that is reflected on an increase in foam volume and collapse time as seen for the 60:40 mineral system. With asphaltene solutions in 70:30 mineral, the foam volume and collapse time increased initially at 1 wt % and it decreased at 2 wt % and remained constant with further increase in concentration up to 5 wt %. On the contrary, resins in 70:30 mineral, appear to exhibit a systematic increase in foam volume and slight increase in collapse time at 5 wt % concentration. The foam volume and collapse time is directly proportional to concentration and bulk viscosity in case of resins. With asphaltenes in 60:40 mineral, they showed the same trend like resins with the formation of small-sized asphaltene aggregates. On the other hand, asphaltenes in 70:30 mineral form large flocs with an appreciable degree of precipitation. The precipitation of AH asphaltenes and the inability of gross flocs and precipitates to adsorb at the interface are believed to cause a decrease in foam volume and collapse time. Alternatively, gross precipitation may simply lead to reticulated particles whose density and shape destabilize the foams.

3.8. Effect of Asphaltenes and Resins Combined.

Experiments were performed in which AH asphaltenes were combined in varying concentrations with 10% AH resins (w/w) dissolved in 60:40 mineral. The foam volumes and collapse times as a function of asphaltene concentration are shown in Figure 9. The foam volume is observed to peak from 1 to 2% asphaltene and, thereafter, decrease with increasing asphaltene concentration. The viscosity of the 10% resin solution in 60:40 mineral is about 4.5 cP (Figure 5C) and the addition of 2% asphaltenes to 60:40 mineral should increase the viscosity by an additional 1–1.5 cP (Figure 1C). Thus

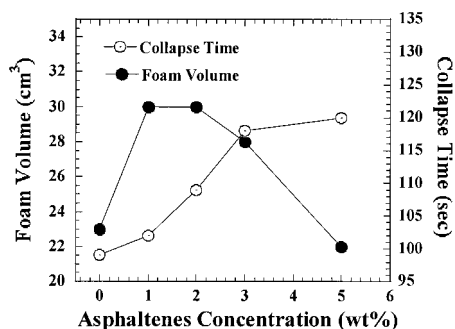


Figure 9. Foam volume and collapse time as a function of AH asphaltene concentration in 60:40 mineral containing 10 wt % AH resins.

the peak in foam volume is seen to be associated with the attainment of the characteristic threshold viscosity of 5.5 cP alluded to above. The collapse time is observed to increase monotonically over the range of asphaltene concentrations, again consistent with the notion that all of the asphaltenes are solvated in solution, available for adsorption, and the viscosity is expected to increase monotonically.

4. Conclusions

A number of significant conclusions can be drawn from this study. Asphaltenes and resins can both contribute independently to crude oil foamability and foam stability. Bulk viscosity is clearly a significant factor and contributes to foam generation and stability; however, it is not the only governing factor. Asphaltene adsorption and state of aggregation governs the stability of asphaltene-stabilized foams. Asphaltenes appear to be most surface-active and generate the most stable foams at solvent conditions nearest the solubility limit. Per unit mass, asphaltenes appear to be stronger stabilizers of foam than resins, despite the fact that resins reduce gas–liquid surface tension to a greater degree than asphaltenes. This is presumably due to the greater elasticity and mechanical rigidity of asphaltenic microstructures at interfaces, as compared to those structures formed by resins. This is consistent with what is observed in water-in-oil emulsion films stabilized by asphaltenes. Beyond the solubility limit, i.e., when asphaltenes have formed flocs and precipitates, foam stability is observed to diminish, presumably either due to a reduction in surface activity of the asphaltenic aggregates, a reduction in the amount of gas–liquid surface area which the asphaltenes can cover, and/or due to the reticulated nature of the asphaltenic flocs which may contribute to foam destabilization. Foam generation and stability appears to be dominated by surface adsorption and bulk viscosity in the case of resins. Solvent aromaticity and resin/asphaltene ratio control asphaltene state of aggregation and thus play a central role in dictating foam stability in solutions comprised of both resins and asphaltenes. The presence of resins appears to render asphaltenes more labile and enhances resulting foam stability.

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