Effects of Asphaltene Solvency on Stability of Water-in-Crude-Oil Emulsions

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The formation of stable and persistent emulsions and foams in the production and refining of crude petroleum is a challenge which has defied broad and generic resolution for several decades. Rational and systematic approaches to demulsification have been slow to develop due to a lack of fundamental understanding of the molecular origins of emulsion stabilization and the full range of factors which govern emulsion stability. Several studies have shown the importance of resins and asphaltenes, which have the ability to organize and form rigid films at the oil/water interface. We have developed a molecular model in which we propose that the integrity of these films and thus their ability to stabilize water-in-crude-oil emulsions are sensitive to a variety of crude solvency parameters, such as aromaticity, resin-to-asphaltene ratio, and polar functional group concentration. This model was tested by correlating the stability of emulsions formed from a variety of crude oils—Arab Berri (Extra Light), Arab Heavy, Alaska North Slope, and San Joaquin Valley—in which the resin and asphaltene contents vary, as well as their specific characteristics. The results of the elemental and functional group characterization of these crude oils and their fractions and the techniques utilized to obtain them were presented previously. Detailed quantitative protocols for gauging relative emulsion stability have been developed to further evaluate the proposed model by blending solvents of varying aromaticity and by doping isolated resins from different crudes into solvent-modified crudes. Dramatic destabilization of emulsions was accomplished by modifying the crude solvency in either fashion. Simple physical and chemical techniques for minimizing emulsion formation such as basic crude blending and solvent-recycle schemes will also be discussed.

INTRODUCTION

Waste minimization and cleanup have become the focus of environmental policies in the petroleum industry (2–8). As a preliminary step during refinery treatment, crude oils are normally desalted to remove species such as chloride salts which poison refinery catalysis and enhance corrosion of overhead distillation columns (9). In this process, water (‘‘wash water’’) is deliberately emulsified into the oil to contact hydrophilic materials, which then partition into the aqueous droplets (10, 11). These desalter emulsions must subsequently be broken down to recover the ‘‘clean’’ crude oil. However, a considerable proportion of these emulsions are very stable and lead to sludge generation (12). As the EPA continues to redefine specific petroleum-derived components which will be targeted as listed wastes, the need to minimize the formation of petroleum emulsions and the impetus to develop new methods for effective treatment of them have become more acute.

Despite years of research, there is a lack of a fundamental understanding of the mechanisms governing the stability of oil-continuous emulsions. With crude oil emulsions, the importance in long-term stability of a rigid and protective film surrounding the water droplets is clear (13–18). The detailed properties of this film, together with a fundamental knowledge of the chemistry of the interfacially active components in the crude oil, are far from understood (19). However, studies have established the significance of components such as asphaltenes and resins, which, because of their surfactant-active and structure-forming properties, accumulate at the interface and hence have pronounced effects on emulsion stabilization and breaking (11, 13–16, 19–31). Others have also shown the importance of other components which may be present in the crude such as waxes and inorganic solids (8, 18, 19, 24, 31–42). The focus of this study will be on the role of the asphaltenes and their interactions with the resins and surrounding crude medium in forming these interfacial films and the resultant effects on emulsion stability. Therefore, it is of interest to isolate and characterize these specific crude oil components.

It has been suggested that the asphaltenes tend to form aggregates which have an adsorbed covering sheet of aromatic resins as a stabilizing layer (43–45). These proposed interactions between the resins and asphaltenes are illustrated in Fig. 1. Strong indications have been obtained that emulsions stabilized by individual asphaltene molecules, which are dissolved in the oil phase in the form of a molecular solution, are of little significance for crude oils, when compared with stabilization by colloidally dispersed asphal-
Asphaltene association is also determined in part by the balance of acidic to basic functional groups within its chemical structure and also that of the resins. It is evident that several fundamental research questions need to be addressed: (i) What key physical properties of the petroleum and contacting water in the refinery dictate the ultimate stability of the emulsion? Asphaltene and resin content? Water pH and ionic strength? (ii) What are the chemical functional groups in the resins and asphaltenes which contribute to their interfacial activity? (iii) What interactions between the interfacially active components (resins and asphaltenes) are responsible for the stability of these emulsions? The answers to these and related questions serve as starting points for development of emulsion destabilization and minimization techniques.

The purpose of this study is to determine the effect of the solvency state of the asphaltenes on the stability of water-in-crude-oil emulsions. An emulsion stabilization mechanism is presented and discussed in which the solvency of the asphaltenes is mediated by the resins and the surrounding crude medium. The state of asphaltene solubility is proposed to be governed by the characteristics (e.g., carbon type and polar functional group content) of each of these components in the distillate part of the crude or residual oil, but they do not dissolve to varying extents when associated with resins. It has been further determined that asphaltenes stabilize water-in-oil emulsions only if they are near or above the point of incipient flocculation, which suggests that their mode of action is to collect at the interface in the form of finely divided solid particles or aggregates. From these studies, it can be inferred that modifying the solvency of the asphaltenes from a state of dispersion to a state of dissolution should decrease the ability of asphaltenes to stabilize emulsions.

Since the resins and asphaltenes in crude oil are known to contain acidic and basic groups, the pH of the water in an emulsion can be expected to affect both the quantities and types of materials constituting the interfacial film. The aqueous-phase pH was indeed found to significantly affect the physical properties of the adsorbed films (e.g., rigidity and mobility), which led to laboratory tests of pH adjustment in emulsion breaking. Several testable hypotheses were formulated from this extensive and in-depth survey of the literature:

- Asphaltenic colloids solvated with resinous material play an important role in emulsion stabilization.
- Adsorption of these components forms films of considerable mechanical strength at the droplet interface and renders the droplet stable to coalescence.
- The state of dispersion of the asphaltenes (molecular vs colloidal) is critical to the strength or rigidity of these films and hence to the stability of petroleum emulsions.

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**EXPERIMENTAL**

**Materials.** The crude oils chosen for this study (Arab Berri, Arab Heavy, Alaskan North Slope, and San Joaquin Valley) were selected because of their extensive use in oil refineries and because they represent extremes in gravity, resin and asphaltene contents, and emulsion-forming tendencies. The general properties of the crude oils selected for this study are presented in Table 1. Arab Heavy (AH) is a high sulfur crude produced from an off-shore field, Safaniya, known to be the world’s largest offshore field (54, 55). Arab Berri (i.e., Arab Berri Extra Light, AB) is a high 30 API gravity, low sulfur crude produced from Upper Jurassic Arab zone reservoirs in Berri, Saudi Arabia (55, 56). The nitrogen-rich San Joaquin Valley (SJV) crude oil (a blend of...
crudes from San Joaquin Valley, California) is a crude of low °API gravity and unusually high viscosity (57). Alaskan North Slope (ANS) is produced from fields in the North Slope of Alaska, predominantly in the Prudhoe Bay region.

Methods. To ensure homogeneity of the oil samples, the whole crudes were mixed thoroughly with the use of a Harbil GQM high-speed paint mixer for 3 min. The aqueous phase (i.e., deionized water) was prepared by adjusting the pH using diluted NaOH and HCl. The emulsions were produced according to a standard protocol outlined in schematic form in Fig. 2. Six milliliters of deionized water (at specified pH) and 4 mL of the whole crude oil were pipetted into a 15-mL polypropylene jar. This mixture was then processed with the use of a Virtishear Cyclone IQ homogenizer with a 6-mm rotor/stator configuration (gap width, 0.127 mm) at 15,000 rpm for 3 min at the oil/water interface, for 2 min at the bottom of the jar, and for 1 min just below the oil/air interface. Immediately after homogenizing, the emulsions were transferred to 10-mL polypropylene centrifuge tubes; most emulsions poured readily immediately following emulsification. The amounts of oil and water to be emulsified (including the W/O ratio), the geometry of emulsifying equipment (e.g., 15-mL jar, 6-mm rotor/stator configuration), and the amount of energy input to the system specified in the emulsification protocol were determined in preliminary experiments to ensure reproducibility, complete emulsification of materials, and droplet size distributions typical of emulsions produced in the refineries (5–50 μm).

Referring again to Fig. 2, the fresh emulsions were then allowed to stand under the influence of gravity for 24 h before the amount of water which separated was determined since a period of rapid coalescence is known to immediately follow the formation of an emulsion (15). The volume of oil and water resolved, if any, after gravitation for 24 h

![FIG. 2. Schematic of the emulsion generation and standard/modified stability protocols.](image-url)
was measured via visual inspection by placing the emulsion samples next to a graduated centrifuge tube. The emulsions were then centrifuged using a RC5C refrigerated centrifuge from Sorvall Instruments at 15,000 rpm (28,700 g) and 30°C for 30 min. The volumes of water and oil separated due to centrifugation were determined by decanting the oil and pipetting the water into separate graduated tubes. The amount of resolved water is the most appropriate gauge of emulsion stability in water-in-crude-oil emulsions since coalescence of the droplet phase is the limiting step in the demulsification process (53).

To study the effects of changes in system variables (e.g., crude oil types, added resins, added solvents of varying aromatic carbon content, etc.), a modified stability protocol was employed which resolved approximately half the water from the whole crudes (i.e., base cases). As shown in Fig. 2, the modified stability protocol simply adds heating and recentrifugation steps to the standard stability protocol to attain the desired water resolution. When the modified protocol was used, the emulsion samples were heated in a water bath to a specified temperature for ~18 h after the initial centrifugation and were then recentrifuged at the previously noted specifications. By changing the amount of heat input into the system between centrifugations, one can control and determine the amount of water resolved for each of the base cases in a particular study. This enables the investigator to broaden the window of observed trends in relative emulsion stability. Preliminary results indicated the standard protocol was sufficient to obtain the desired water resolution (~50%) for Alaskan North Slope crude, while Arab Berri and Arab Heavy crudes required heating to 45 and 70°C, respectively, and recentrifugation.

The crude oils under investigation were fractionated according to their resin and asphaltene contents and were subsequently characterized with respect to their elemental, functional group, and aromatic carbon contents in a prior study. The instruments and techniques used to obtain the compositional analysis of these crudes are described in a previous paper (1).

RESULTS AND DISCUSSION

Effect of crude type. The emulsion stability results for the types of crude oils in this study which formed emulsions stable to gravity sedimentation are presented as a function of both crude type and aqueous-phase pH in Fig. 3. It should be noted that emulsion stability, according to this operational definition, increases as the amount of resolved water decreases (i.e., they are inversely related). It is apparent that Arab Heavy forms the most stable emulsions (0–5% water resolved, except at basic pHs 10 and 12) and that Arab Berri and Alaska North Slope form considerably weaker emulsions (50–90% water resolved). San Joaquin Valley crude formed emulsions which were totally unstable to gravity sedimentation (i.e., all of the water resolved after gravity for 24 h). This was thought to be due to its high viscosity at room temperature, which inhibits the shearing of water droplets to the micrometer-level droplet sizes necessary to form a stable emulsion. Attempts to form an emulsion with SJV at a temperature of 100°C were successful to some extent. The heating of the SJV crude oil to 100°C would be sufficient to melt any paraffinic and/or microcrystalline waxes present in the crude and consequently lower the viscosity of the continuous oil phase enough to allow intimate mixing of the oil and water. However, these emulsions were still not very stable (approximately half the water resolved after settling under gravity for 24 h) compared to the emulsions formed from the other crudes in this study at room temperature. An emulsion formation and stability protocol which allows analysis at higher temperatures and pressures is currently being developed. With this in mind, the stability of emulsions produced from these crudes in order of decreasing rank are as follows:

Arab Heavy > Arab Berri > Alaska North Slope > San Joaquin Valley.

Effect of aqueous-phase pH. As depicted in Fig. 3, aqueous-phase pH affected emulsion stability markedly. With AH and AB crudes, emulsions prepared with water at pH 10 and 12 were relatively unstable. The polar functional groups contained in the resinous and asphaltene material originally present in the interfacial film would most likely be ionized at these extreme pH values. The ionization of these polar groups would be capable of creating high surface charge densities that would drastically change the film properties by introducing an internal repulsion in the film, thereby destroying the mechanical properties that give rise to protection against coalescence. The restored or enhanced stability observed in AB and AH emulsions at low pHs reveals the
ous phase upon emulsification. These results of the effects of varying aqueous-phase pH suggest that these acidic compounds are more effective at stabilizing emulsions when they are not ionized.

Proposed mechanism of emulsion stability. Before we can attempt to relate the observed trends in the stability of the emulsions produced from the crude oils in this study to certain characteristics of these crudes, we must consider how the polar, surface-active constituents of the crude (e.g., resins and asphaltenes) interact with each other and with the surrounding crude medium and how these interactions could affect the resultant emulsion stability. As mentioned in the literature review, resins help to solubilize the asphaltenes by forming a resin-solvated asphaltenic aggregate (illustrated in Fig. 1) and thus tend to diminish the surface-active nature of the asphaltenes. However, as depicted in Fig. 5, these resin-solvated asphaltenic colloids might be able to lower their free energy by ‘‘shedding’’ the solvating resins on one potential absence of strongly basic polar groups in these particular crude oils.

Also, the water resolved when the crude emulsions are subjected to centrifugation and/or heating was characterized with respect to pH. This ‘‘residual’’ aqueous-phase pH is plotted as a function of its initial pH for ANS and AB in Fig. 4. For neutral and basic pHs, the residual aqueous-phase pH is consistently and substantially more acidic than the initial pH by as much as 4–5 pH units for all the crudes studied. This suggests that the interfacially active compounds in the crude adsorbed at the oil/water interface are acidic in nature and some ionize or dissociate into the aque-
in solvating resins relative to its asphaltene content (i.e., a crude oil which has a high resin-to-asphaltene, R/A, ratio), we would expect the asphaltenes in this particular crude oil to be molecularly dissolved and therefore unable to stabilize emulsions. Aside from the resin-to-asphaltene ratio, there are at least two other characteristics that merit consideration: (i) Asphaltenes are known to be the most aromatic portion of the crude oil; therefore we would expect that as the aromaticity of the resins and surrounding oil medium increased with respect to the aromaticity of the asphaltenes, the asphaltenes would become more molecularly dissolved and less able to stabilize emulsions. (ii) Hydrogen-bonding interactions between the resins and asphaltenes could enhance solvation of the asphaltenes. It stands to reason that if the asphaltenes from a particular crude oil contain high concentrations (relatively speaking) of C==O groups and if the corresponding resin fraction is rich in carboxylic acid or other proton-donating polar functional groups, then intermolecular hydrogen bonding could lead to strong solvation of asphaltenes by resin molecules. The higher the concentration and polarity of these functional groups, the stronger the interactions between them, thus diminishing the ability of these colloidal aggregates to shed their sheath of solvating resins in order to become surface-active.

Apparently, then, the solubility of asphaltenes in crude oil, their tendency to aggregate, and their tendency to adsorb at oil/water interfaces should be controlled by: (i) the ratio of resins to asphaltenes, (ii) the aromaticity ratios of the resins and the crude medium to the asphaltenes (as defined in Fig. 7), and (iii) the concentrations of the polar functional groups (e.g., carbonyls, carboxylic acids, pyrroles, amides, and phenols) contained in the resin and asphaltene fractions of a given crude. These three modes of asphaltene solvation are illustrated in Fig. 6, in which the properties which determine the extent of asphaltene solvation and their resultant surface activity are highlighted. The difference in properties shown in Fig. 6 could either be borne out in a comparison of two different crude types or effected through chemical addition in a given crude oil. These assertions also suggest possible means for emulsion minimization and/or resolution. The asphaltenes would become less surface-active with the increasing availability of solvating resins (at higher R/A values) whether through chemical addition or as a function of crude type. Increasing the aromaticity (i.e., aromatic carbon content) of the crude medium through the addition of aromatic solvents should solvate strongly surface-active asphaltenes by creating an environment that is more "like" the nature of the condensed, polyaromatic asphaltene molecules. This in effect increases the aromaticity ratio of the crude medium with respect to the asphaltenes. Finally, a crude oil which has a high polar functionality (i.e., high concentration of functional groups) in its resin and asphaltene molecules should form asphaltenic colloidal aggregates which are more strongly solvated through the increased number of H-bond interactions with the resin molecules than a crude oil of lower functional group content. Thus, the crude oil composed of resins and asphaltenes of high functionality would contain asphaltenic aggregates that find it difficult to shed their solvating resins and are consequently less surface-active and have a lower propensity to form stable emulsions. Of course, each of these contributions is not isolated from the other in determining the solubility state of the asphaltenes within a given crude oil. In fact, one could also envision combining some or all of these ideas such as the addition of resin molecules, which are both very aromatic and highly functional, into a particular crude to molecularly dissolve the indigenous asphaltenes and minimize the formation of stable emulsions during processing.

The results of the effect of the different crude types on emulsion stability are reviewed and the anticipated correlations between the characterization parameters of the crudes under study and their observed emulsion stabilities are summarized in Fig. 7. Note that all of these parameters are expected to be inversely related to the emulsion stability according to the proposed mechanism.

Discussion of characterization results. With this in mind, the yields and pertinent characterization results of the polar fractions isolated from these crudes are presented in
Emulsion Stability Results by Crude Type:

Arab Heavy > Arab Berri ≥ Alaska North Slope > San Joaquin Valley

Effects of Proposed Mechanism:

1. The intensities of the aromatic carbon ring-breathing modes (at ~1600 cm⁻¹) are very sensitive to the polarity of aromatic substituent groups. Therefore, the apparently high aromatic carbon content of SJV polar fractions (as measured by FTIR spectroscopy) is likely an artifact of the strong polarity of these fractions, as indicated by the polar functional group content already cited. While this might seem to give rise to fractions which are more surface-active in SJV than in AH, the increased polarity may actually cause the asphaltenes in SJV to be more strongly solvated by the resins and thus less surface-active as discussed previously. Other distinctive features of the SJV polar fractions were the H/C ratio and the aromatic carbon content of the asphaltene fraction. The H/C ratio of the SJV asphaltenes was considerably higher than those from the other crude samples (1.17 vs 1.02–1.11), and the aromaticity value was lower (46% vs 49–55%). These results suggest either that SJV crude has more oils and summary of anticipated effects of the proposed mechanism on aliphatic character (less fused polyaromatic ring structure) than other crude oils or that the asphaltene fraction still contains some strongly adsorbed resinous compounds. In either case, the SJV polar fractions would likely be less capable of stabilizing emulsions than the polar fractions of the other crudes, which was indeed found to be the case in this study.

Correlation of R/A and asphaltene contents with emulsion stability. The R/A value and asphaltene contents of the four crudes in this study (in order of increasing emulsion stability) are presented graphically in Fig. 8. It is evident that Arab Heavy has the lowest R/A value and is also richest in asphaltenes, as would be expected from the proposed stabilization mechanism. However, AB has the highest R/A value but forms the second most stable emulsion. The R/A value definitely tells us part of the “story,” but it is obvious that one cannot depend solely on this parameter as a predictor of relative emulsion stability.

Effect of addition of resins on emulsion stability. To see a more direct and comprehensive effect of the R/A value

Table 2. These results were compiled from a previous study (1). The fractionation was performed using a method similar to the SARA technique which employs precipitation of asphaltenes with heptane followed by chromatographic isolation of resins. Characterization of the polar fractions by elemental analysis and by FTIR spectroscopy revealed that AH asphaltenes were richest in sulfur and considerably lower in oxygen content and carbonyl functional group content than SJV crude. These results reveal that the concentrations of carboxylic/carbonyl and pyrrolic functional forms are 1.5–3 times larger in SJV polar fractions than in AH polar fractions, indicating that SJV polar fractions are considerably more acidic and polar. Additionally, the aromatic carbon content of the SJV asphaltenes as measured by FTIR spectroscopy was much higher than the “true” value obtained via NMR spectroscopy. As discussed in a previous paper.

Effect of addition of resins on emulsion stability. To see a more direct and comprehensive effect of the R/A value

### Table 2

Summary of Characterization Analysis of Resins and Asphaltenes Isolated via Precipitation and Extrography

<table>
<thead>
<tr>
<th>Characterization parameter</th>
<th>SJV</th>
<th>ANS</th>
<th>AB</th>
<th>AH</th>
<th>SJV</th>
<th>ANS</th>
<th>AB</th>
<th>AH</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Yield</td>
<td>20.26</td>
<td>9.47</td>
<td>3.49</td>
<td>9.56</td>
<td>4.57</td>
<td>3.35</td>
<td>0.68</td>
<td>8.27</td>
</tr>
<tr>
<td>H/C</td>
<td>1.38</td>
<td>1.38</td>
<td>1.36</td>
<td>1.39</td>
<td>1.17</td>
<td>1.08</td>
<td>1.02</td>
<td>1.11</td>
</tr>
<tr>
<td>% N</td>
<td>1.89</td>
<td>0.94</td>
<td>0.67</td>
<td>0.66</td>
<td>2.44</td>
<td>1.11</td>
<td>0.77</td>
<td>0.94</td>
</tr>
<tr>
<td>% S</td>
<td>1.90</td>
<td>3.29</td>
<td>4.76</td>
<td>5.95</td>
<td>1.60</td>
<td>3.06</td>
<td>5.84</td>
<td>7.17</td>
</tr>
<tr>
<td>% O</td>
<td>2.30</td>
<td>2.91</td>
<td>2.44</td>
<td>2.39</td>
<td>3.52</td>
<td>2.67</td>
<td>2.49</td>
<td>1.46</td>
</tr>
<tr>
<td>% Arom. C (NMR)</td>
<td>38.7</td>
<td>38.1</td>
<td>38.8</td>
<td>37.9</td>
<td>45.9</td>
<td>51.9</td>
<td>54.8</td>
<td>49.2</td>
</tr>
<tr>
<td>% Arom. C (FTIR)</td>
<td>17.0</td>
<td>11.9</td>
<td>11.7</td>
<td>18.4</td>
<td>62.8</td>
<td>38.2</td>
<td>46.9</td>
<td>28.7</td>
</tr>
<tr>
<td>% Carbonyl</td>
<td>2.3</td>
<td>1.5</td>
<td>1.7</td>
<td>1.3</td>
<td>1.5</td>
<td>1.0</td>
<td>1.7</td>
<td>0.6</td>
</tr>
<tr>
<td>% Pyrrole</td>
<td>0.6</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.5</td>
<td>0.2</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>V (ppm)</td>
<td>187.7</td>
<td>117.9</td>
<td>62.8</td>
<td>205.0</td>
<td>463.8</td>
<td>516.4</td>
<td>352.8</td>
<td>667.6</td>
</tr>
<tr>
<td>Ni (ppm)</td>
<td>268.0</td>
<td>64.4</td>
<td>43.0</td>
<td>85.8</td>
<td>873.1</td>
<td>386.0</td>
<td>130.5</td>
<td>352.1</td>
</tr>
</tbody>
</table>
on emulsion stability, we explored the option of adding or “doping” of resins to the crude oil. This study has been performed with most combinations of crude types plus resins from different crude types dissolved in heptol (to ensure complete dissolution of the resin fraction within the crude oil) to gain further insight into the interactions between these interfacially active constituents in the presence of the indigenous crude oil. The effect of adding resins from AH, AB, and SJV to solvent-modified AH crude oil (30% v/v heptol in crude oil) using the modified protocol at 50°C as a function of R/A is presented in Fig. 9. The added AH resins destabilize the emulsion appreciably as the R/A is raised from 1.1 to 2.1 and then appears to have little effect thereafter. However, the addition of AB resins, which are relatively higher in sulfoxide content, appears to have a more dramatic and consistent destabilizing effect over the entire range of R/A values up to 3.7. Adding SJV resins, which are rich in pyrolic and carboxylic functional groups, has the most dramatic destabilizing effect when the R/A value is raised from 1.1 to 2.2. It is obvious that resins isolated from different crude types have varying impacts on the resultant emulsion stability, which is exactly what we would expect based on the proposed mechanism.

Effect of addition of solvents on emulsion stability. The hypothesis that asphaltene solvency is directly responsible for emulsion stability led to another study aimed at determining the effect of changing the aromatic nature of the crude medium by blending solvents of varying amounts and aromaticity with the whole crude oils. In our first experiment, crude oils were systematically modified by addition of a purely aliphatic solvent (n-heptane), an aromatic solvent (toluene), or a mixture of the two (70% n-heptane and 30% toluene, so-called heptol) in increasing amounts (10–50%). Figure 10 shows the effects of blending the three different solvents with AB and AH (prior to homogenization), respectively, on emulsion stability as a function of the solvent content in the oil phase. It is clear that addition of toluene and heptol destabilizes the emulsions, while with sufficient addition of n-heptane (30–50%), the emulsions are actually stabilized. This is fully consistent with the notion that increased aromaticity of the crude medium helps to further solubilize the asphaltenes. Moreover, with heptol and toluene, there may be a viscosity reduction effect. With n-heptane, however, it is clear that the stabilization of the emulsion must be due to reduced molecular solubility of the asphaltene fraction of the crude. Despite the fact that 30% added n-heptane is clearly not sufficient to precipitate the asphaltenes, there must be reduced molecular solubilization resulting in aggregation and surface activity.

Extent of effect of toluene blending and pH adjustment. Since the blending of toluene had the greatest destabilizing effect on the stability of emulsions produced from AB (e.g., complete resolution at 30% toluene) as determined by the modified protocol at 45°C, an aqueous-phase pH scan with a 30% blend of toluene was performed to determine the water resolution attained solely by gravity sedimentation since this is the most practical method utilized in the refineries. The results in Fig. 11 show that the emulsions produced with the crude/toluene blend are stable under gravity for acidic and neutral pHs (pH 2–8), but exhibit significant water resolution (~70%) for basic pHs (pH 10–12). No water resolution from AB crude emulsions without added toluene is observed after the emulsion was allowed to settle under gravity; therefore, this result suggests that solvent-modified AB emulsions could be broken or even prevented from forming simply by controlling the pH of the aqueous phase.
FIG. 10. Effect of blending solvents (prior to homogenization) of varying aromaticity on the stability of emulsions produced from Arab Berri and Arab Heavy.

Effects of solvent aromaticity and molecular structure. Solvents of varying molecular structures and aromaticities— including benzene, toluene, xylene, ethylbenzene, tert-butylbenzene, cumene, and cymene—were also utilized to further gauge the influence of the solvent “power” on emulsion stability as mediated by the state of dispersion of the asphaltenes in the crude medium. The results from this study are plotted in Fig. 12 as a function of the amount of solvent added to AH crude oil prior to homogenization. It is evident that all of the solvents are sufficiently aromatic to destabilize the emulsions and moreover that the most aromatic solvents (i.e., solvents of highest aromatic carbon content) are more effective in resolving the emulsions. To see this effect more clearly, the slopes of these water resolution curves for the various solvents (at the onset of destabilization, \( \approx 15\% \)) were plotted as a function of the solvent aromaticity as presented in Fig. 13. There is a definite trend toward greater destabilization effectiveness as the molecular aromaticity of the solvent increases. Since asphaltenes are known to be condensed polyaromatic-ringed compounds, naphthalene and phenanthrene were dissolved in benzene (at concentrations just under their solubility limits of 0.37 and 0.35 g/mL of benzene, respectively) to see if this would effect any further destabilization of the emulsions produced with these solvent-modified crudes. This was indeed found to be the case, as Fig. 12 shows a considerable destabilization over and above what was observed with the other pure solvents over the entire range of added solvent.

Summary of correlation between crude oil characteristics and their resultant emulsion stability. In summary, the results from the characterization of these crudes in terms of asphaltene content, R/A, the aromaticity ratios of the crude
the effect of the very low value of the aromaticity ratio of the oil to the asphaltenes in this particular crude. From the solvent experiments just presented, the low aromaticity of the AB crude medium with respect to the aromaticity of its asphaltenes would be expected to play a large role in stabilizing emulsions produced from this crude oil. Therefore, even though there does not appear to be a single, universal parameter to predict emulsion stability, there is preliminary evidence to support the utility of a phase map or model which includes some or all of these parameters in predicting relative stability of emulsions produced from different crude oils.

**CONCLUSIONS**

The results from this study tend to support the proposed mechanism in which emulsion stability is governed primarily by the state of solubility of the asphaltenes in the crude oil. Assertions from the literature stipulate that asphaltenes which are at or near the point of precipitation are more surface-active than those which are sufficiently solvated or molecularly dispersed. The characteristics of the crude oil which should play a role in determining the solubility state of the asphaltenes include the resin-to-asphaltene ratio, the aromaticity ratios of the crude medium and resins with respect to the asphaltenes, and the concentration of polar functional groups in the resins and asphaltenes. These parameters were tabulated and correlated with the stability of the emulsions produced from these crude oils. The observed trends suggest that a model which incorporates some or all of these parameters (and possibly others) could be utilized to predict relative emulsion stability.

This research also suggests a number of possible emulsion minimization approaches in the refinery which could be implemented at relatively low cost. One obvious possibility is the blending of crudes to achieve crude aromaticity and/or R/A values which yield minimal stability emulsions. For example, when SJV is blended with AH crude in proportions exceeding 30% SJV, the resulting blended crude forms very

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**TABLE 3**

<table>
<thead>
<tr>
<th>Crude type</th>
<th>Increasing emulsion stability</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SJV whole</td>
</tr>
<tr>
<td>Asphaltene content^a</td>
<td>4.57</td>
</tr>
<tr>
<td>R/A</td>
<td>4.43</td>
</tr>
<tr>
<td>Arom. oil/arom. asphaltenes^b</td>
<td>0.45</td>
</tr>
<tr>
<td>Arom. resins/arom. asphaltenes^b</td>
<td>0.84</td>
</tr>
<tr>
<td>% Polar functional groups^c</td>
<td>4.44</td>
</tr>
</tbody>
</table>

^a Wt%.
^b As determined by 13C NMR spectroscopy.
^c Wt% of total asphaltenes and resins as determined by FTIR spectroscopy.
unstable emulsions in our laboratory which settle upon the action of gravity. Another straightforward implementation of the results of this research would involve the blending of aromatic distillation side streams either into the desalting unit or into a desalter knockout tank in order to solubilize adsorbed asphaltenes and destabilize emulsions. Another option that could be implemented in conjunction with these approaches is the adjustment of the wash water pH to an optimum pH, which varies from crude to crude, for which the resultant emulsion exhibits minimum stability. In this study, both AB and AH crude emulsions were destabilized at basic pHs (pH 10–12). Adjustment of aqueous-phase pH is less expensive than many other demulsification methods, such as the use of surfactants, and can appreciably reduce the requirements of more complex and expensive processes needed to achieve the desired resolution of crude oil emulsions in the refineries.

Further questions remain. How general are the results of the research reported here? What effect would temperature and pressure changes have upon the stability of emulsions produced from the crudes in this study, particularly with crudes of high wax contents? How critical is the role of asphaltenic polarity in affecting asphaltene solubility? What more insightful techniques are available to isolate and measure the polarity of these surface-active components? Are there hidden variables which also play an important role in asphaltene solubility, such as molecular weight? Does the minimization of emulsion stability formed from whole crudes by solubilizing asphaltenes result in an enhancement of emulsion stability as formed by adsorption of crude surface-active materials on ultrafine particulates, such as iron oxides or silica? Can phase maps of crudes be created in which aromaticity, asphaltene and resin contents and asphaltene polarity are the key variables in which emulsion stability can be identified as clear regimes on the map? Is it more advantageous to solubilize asphaltenes and carry them with the crude into the catalytic cracking unit or is it preferable to remove them in a desalter emulsion unit and deal with them separately? These questions combine molecular-level thinking with process considerations and constitute a fruitful area for ongoing research.

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REFERENCES
