

# Effects of Asphaltene Aggregation in Model Heptane–Toluene Mixtures on Stability of Water-in-Oil Emulsions

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As part of an ongoing investigation into the stability of water-in-crude oil emulsions, model oils have been utilized to further probe the effects of crude solvency as well as specific resin–asphaltene interactions on emulsion stability. These model oils were constructed by dissolving varying amounts of resins and/or asphaltenes in a mixture of heptane and toluene. The resins and asphaltenes used in this study were isolated from four different crude types—Arab Berri (AB), Arab Heavy (AH), Alaska North Slope (ANS), and San Joaquin Valley (SJV)—and characterized in a previous study using heptane precipitation of the asphaltenes followed by an extrographic separation of the resins from silica gel. Asphaltenes dissolved in heptol at concentrations of just 0.5% were shown to generate emulsions which were even more stable than those generated from their respective whole crude oils. Some types of resins (e.g., from AH and SJV) also demonstrated an ability to stabilize emulsions although these resin-stabilized emulsions were considerably less stable than those prepared with asphaltenes. The primary factors governing the stability of these model emulsions were the aromaticity of the crude medium (as controlled by the heptane:toluene ratio), the concentration of asphaltenes, and the availability of solvating resins in the oil (i.e., the resin/asphaltene or R/A ratio). The model emulsions were the most stable when the crude medium was 30–40% toluene and in many cases at small R/A ratios (i.e.,  $R/A \leq 1$ ). This strongly supports the theory that asphaltenes are the most effective in stabilizing emulsions when they are near the point of incipient precipitation. The types of resins and asphaltenes used to construct these model oils also played a role in determining the resultant emulsion stability which indicates the importance of specific resin–asphaltene interactions. The interfacially active components that stabilized these model systems were the most polar and/or condensed portions of the resin and asphaltene fractions as determined by elemental and neutron activation analyses. All of these results point to the significance of the solubility state of the asphaltenes in determining the emulsifying potential of these crude oils. © 1997 Academic Press

## INTRODUCTION

In an earlier study on the investigation of water-in-crude oil emulsions (1), we developed a molecular model which

brought together what we thought and what has been shown in many literature studies to be the primary contributors to the solubility state of asphaltenes which in turn should have a pronounced effect on the stability of these emulsions. Asphaltenes are in fact reported to stabilize emulsions to the greatest extent when they are at or near the point of precipitation (2–4). It is also well known that the solvency state of petroleum asphaltenes is primarily governed by their interactions with the resins and the surrounding crude medium (5–13). In our conceptual model, we proposed that these interactions are dominated and determined by the availability of solvating resins, the extent of hydrogen bonding between the asphaltenes and resins, and the aromatic solvency of the resins and of the saturates and aromatics in the crude medium itself. We then proceeded to test the sensitivity of these interactions on the stability of emulsions produced from four different crude oils—Arab Berri (AB), Arab Heavy (AH), Alaska North Slope (ANS), and San Joaquin Valley (SJV). In this previous study on whole crude oils, we were able to show to a limited extent that crude solvency parameters such as the R/A ratio, the aromaticity of the solvating crude components, and the polar functionality of the resins and asphaltenes play an important role in determining emulsion stability.

In this study, we have continued our investigation of the stability of water-in-crude-oil emulsions by harnessing the utility of so-called model oils. These model oils were constructed from the resins and asphaltenes isolated from these same four crude oils and were then emulsified with water to gain further insight into the effects of changes in crude solvency and resin–asphaltene interactions on the resultant emulsion stability. One of the goals of studying these model emulsions was to show that the resin and asphaltene fractions are capable of stabilizing water-in-oil emulsions even without other stabilizers such as inorganic solids and waxes. But the principal advantage was that instead of investigating the whole crude oils, attention could be focused on the characterization of the resins and asphaltenes and their specific impact on emulsion stability. Constructing these model oils allowed much greater flexibility in controlling the solubility of the

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**TABLE 1**  
**Summary of Characterization Analysis of Resins and Asphaltenes Isolated via Precipitation + Extrography**

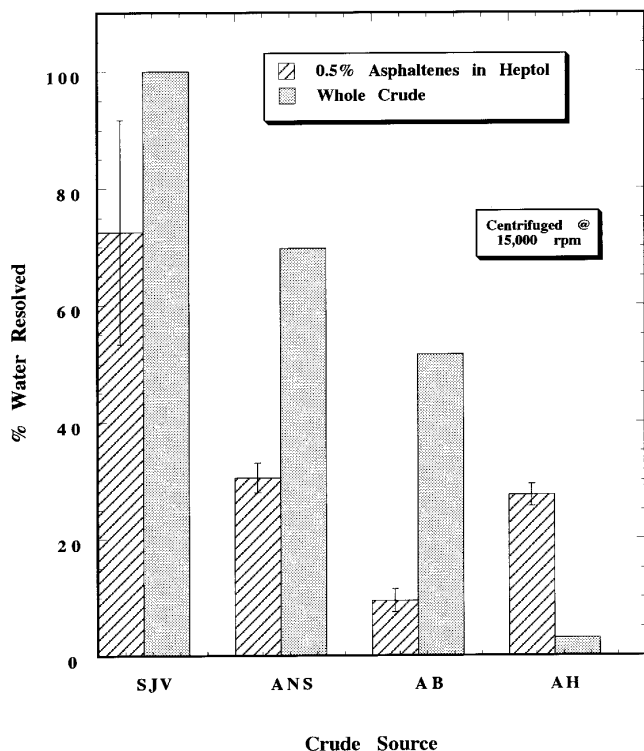
Characterization parameter	Resins				Asphaltenes			
	SJV	ANS	AB	AH	SJV	ANS	AB	AH
% Yield	20.26	9.47	3.49	9.56	4.57	3.35	0.68	8.27
H/C	1.38	1.38	1.36	1.39	1.17	1.08	1.02	1.11
%N	1.89	0.94	0.67	0.66	2.44	1.11	0.77	0.94
%S	1.90	3.29	4.76	5.95	1.60	3.06	5.84	7.17
%O	2.30	2.91	2.44	2.39	3.52	2.67	2.49	1.46
% Arom C (NMR)	38.7	38.1	38.8	37.9	45.9	51.9	54.8	49.2
% Arom C (FTIR)	17.0	11.9	11.7	18.4	62.8	38.2	46.9	28.7
% Carbonyl	2.3	1.5	1.7	1.3	1.5	1.0	1.7	0.6
% Pyrrole	0.6	0.3	0.3	0.3	0.5	0.2	0.2	0.1
V (ppm)	187.7	117.9	62.8	205.0	463.8	516.4	352.8	667.6
Ni (ppm)	268.0	64.4	43.0	85.8	873.1	386.0	130.5	352.1

asphaltenes, which is known to be a primary influence on emulsion stability, since characterization parameters (e.g., resin and asphaltene types and contents and the aromaticity of the crude medium) could be predetermined during construction instead of merely being modified from the original whole crude. This method offers a means for clarifying certain features of the interaction of resins with asphaltenes and

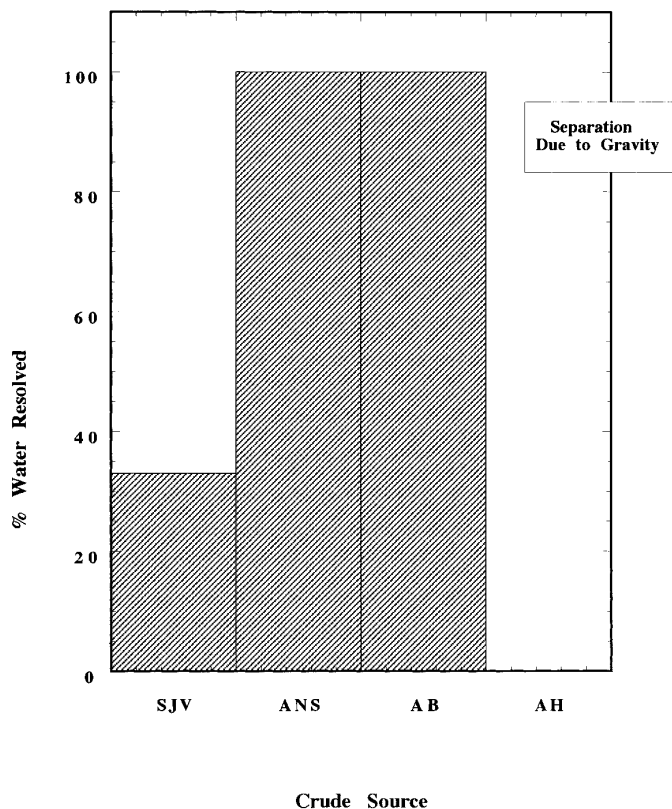
for defining more precisely a criterion for the emulsifiability of crude oils.

### EXPERIMENTAL

The model crudes were constructed using the resin and asphaltene fractions derived from a fractionation method ap-



**FIG. 1.** Impact of asphaltenes from different crudes on emulsion stability (% water resolved) of model systems (heptol, asphaltenes, and water); comparison with whole crude-water emulsion stability.



**FIG. 2.** Effect of resins from different crudes on emulsion stability of model oils: 0.5 wt% resins in n-heptane.

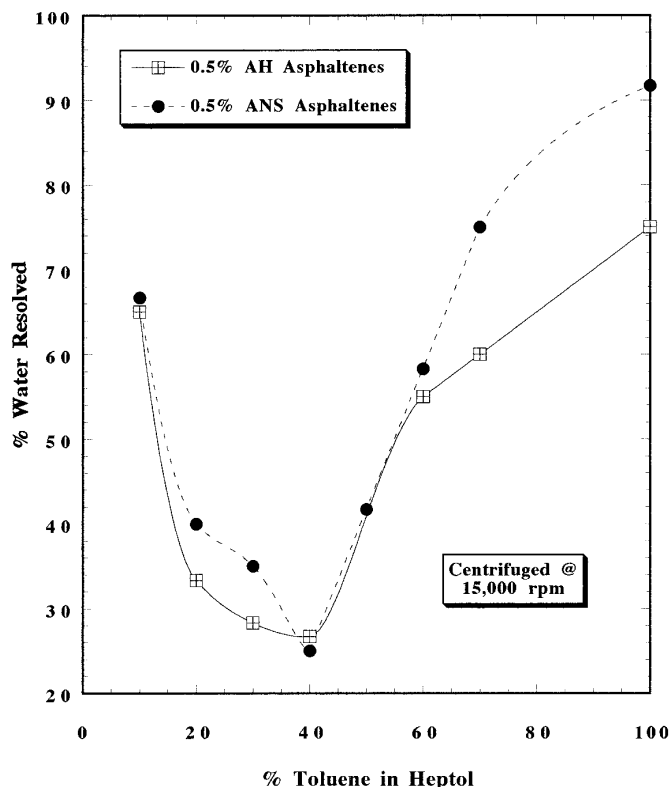


FIG. 3. Effect of aromaticity (% toluene in heptol mixtures) on emulsion stability of 0.5 wt % asphaltenes in heptol mixed with water; AH and ANS asphaltenes, emulsions centrifuged at 15,000 rpm.

plied to four different crudes which were characterized in a previous study (14). Briefly, the asphaltenes were precipitated from the crude oil 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. The four crudes under investigation were Arab Berri (Extra Light), Arab Heavy (AH), Alaska North Slope (ANS), and San Joaquin Valley (SJV).

The resin and asphaltene fractions from these crudes were typically dissolved in 4.4 mL of heptol (7:3 heptane:toluene, unless otherwise noted), both as separate entities and in various combinations and ratios, to study the possible synergistic effects of these fractions. In order to enhance dissolution of these polar materials, the asphaltenes were first crushed into fine particulates with the use of a metal spatula. Appropriate amounts of these fractions were weighed on a Mettler AE 166 Deltarange Balance. The resins and asphaltenes were dissolved separately in 1.3 mL of pure toluene and 3.1 mL of pure heptane, respectively, in 15 mL polypropylene jars. The solvents used were the purest HPLC grade available. Both jars were shaken at the lowest setting on a Fisher Genie 2 Vortex mixer for at least 5 min. The resin solution was then added to the asphaltene solution, and the

mixture was then shaken again for another 5 min before emulsification with 6.6 mL of DI water at pH 6.

The formation of these model emulsions was carried out in the same manner as previously described for the whole crude oils (1). All of the emulsions formed in this study were of the w/o type. Their stability was determined by the amount of water resolved after a 24-h gravitation period, if any, and then again after centrifugation at various field strengths for 30 min. Most emulsions were centrifuged at 15,000 rpm (28,700 g).

The interfacially active components remaining in the unresolved emulsion phase, as well as those found in the creamed oil phase, were isolated by carefully decanting the oily organic phase before evaporating the water and/or heptol from each of the phases for 24 h in a nitrogen-flushed vacuum oven at 70°C. Elemental and neutron activation analyses were then utilized to obtain C, H, N, S, V, and Ni contents in the characterization of these isolated polar components. Details of these characterization techniques were presented previously (14).

## RESULTS AND DISCUSSION

*Effect of asphaltene and resin type.* At the outset, it was necessary to determine the amount of asphaltenes and/or resins

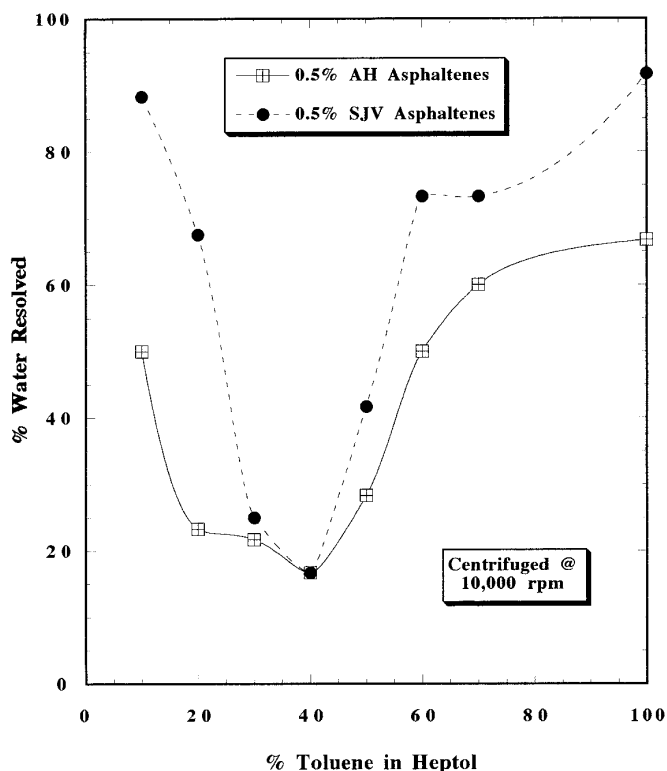
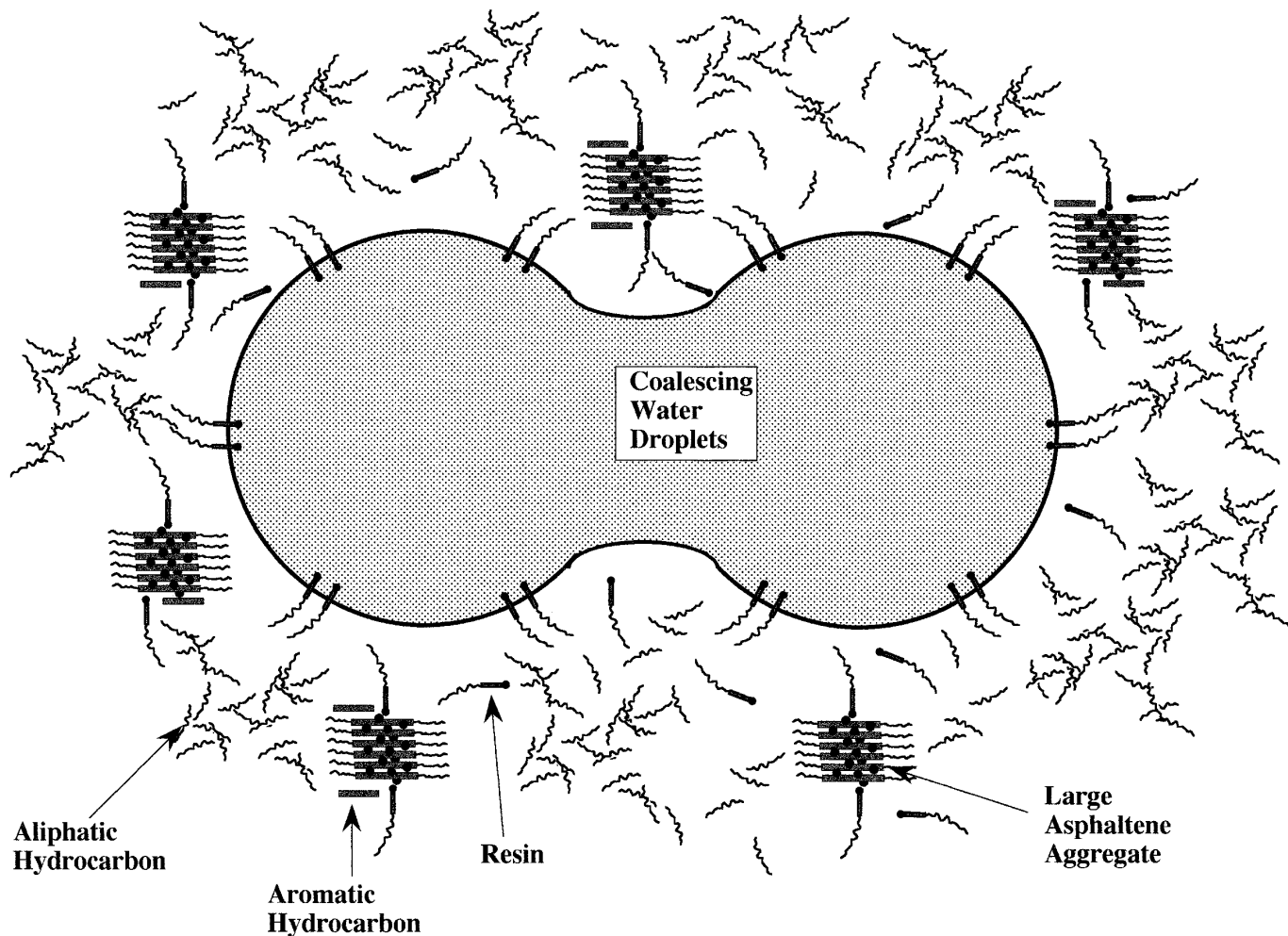


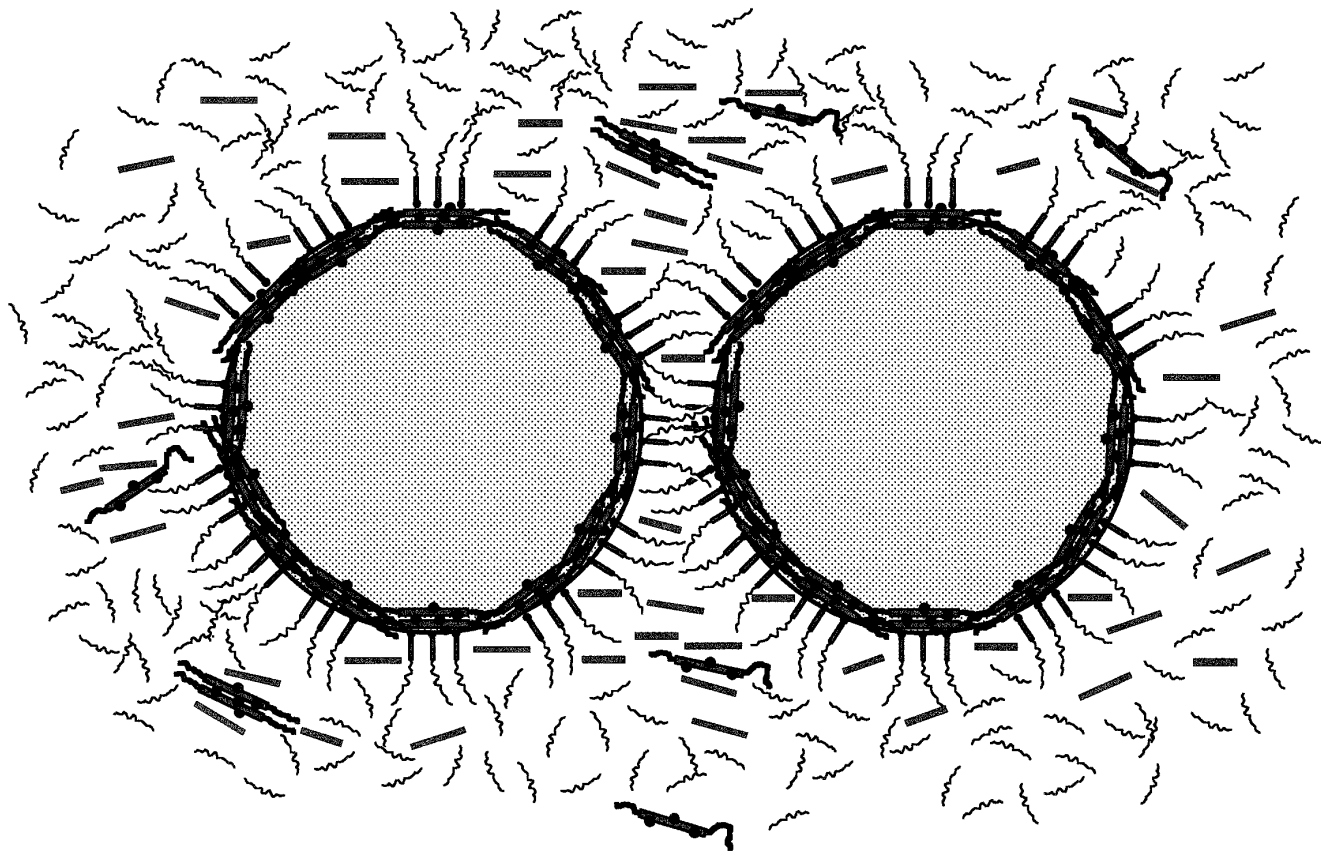
FIG. 4. Effect of aromaticity (% toluene in heptol mixtures) on emulsion stability of 0.5 wt % asphaltenes in heptol mixed with water; AH and SJV asphaltenes, emulsions centrifuged at 10,000 rpm.



**FIG. 5.** Effect of oil aromaticity on asphaltene state of aggregation and resulting interfacial activity: low aromaticity (<20% toluene-in-heptol). Note that droplets coalesce and phase separate due to inability of bulky asphaltene aggregates to adsorb and stabilize the interface.

required to form emulsions which exhibit stabilities similar to those produced from the whole crudes. The results from the characterization of the resins and asphaltenes in these crude oils and from the emulsion stability studies conducted on the whole crudes are presented in Table 1 and Fig. 1, respectively. Also shown in Fig. 1, model oils with asphaltene contents as low as 0.5% are sufficient to form emulsions which are actually more stable, in some cases, than those formed from their respective whole crudes. In fact, in this study, AH is the only crude for which the model emulsion is less stable than the emulsion produced from its whole oil. All of the model emulsions shown in this figure were completely stable to gravity settling (i.e., no water resolution). For SJV, this is in stark contrast to its whole oil, which would almost completely resolve immediately following emulsification at room temperature. Our ability to produce a stable emulsion from the model oil with SJV asphaltenes is most likely due to the diminished presence of micro-

crystalline waxy compounds, which are found throughout the heptane-soluble portion of SJV whole crude. This is in contrast to the purely paraffinic nature of the waxes found in the other three crudes. In addition to their intense viscosifying effect at ambient temperatures which prevents effective shearing of the water droplets, these microcrystalline waxes likely inhibit the emulsifying propensity of the whole crude by confining the interfacially-active compounds within their crystalline structure upon cooling. This severely limits their ability to adsorb and stabilize the water-oil interface simply due to the bulkiness of the amorphous crystals. The differences in the stabilities observed for ANS and AB model and whole emulsions are most likely due primarily to the solubilizing presence of the resins in the whole crude. The AH model emulsion is less stable than its whole counterpart, probably as a result of the large discrepancy in the asphaltene concentration between the two oils (0.5% vs 8.3%, respectively).

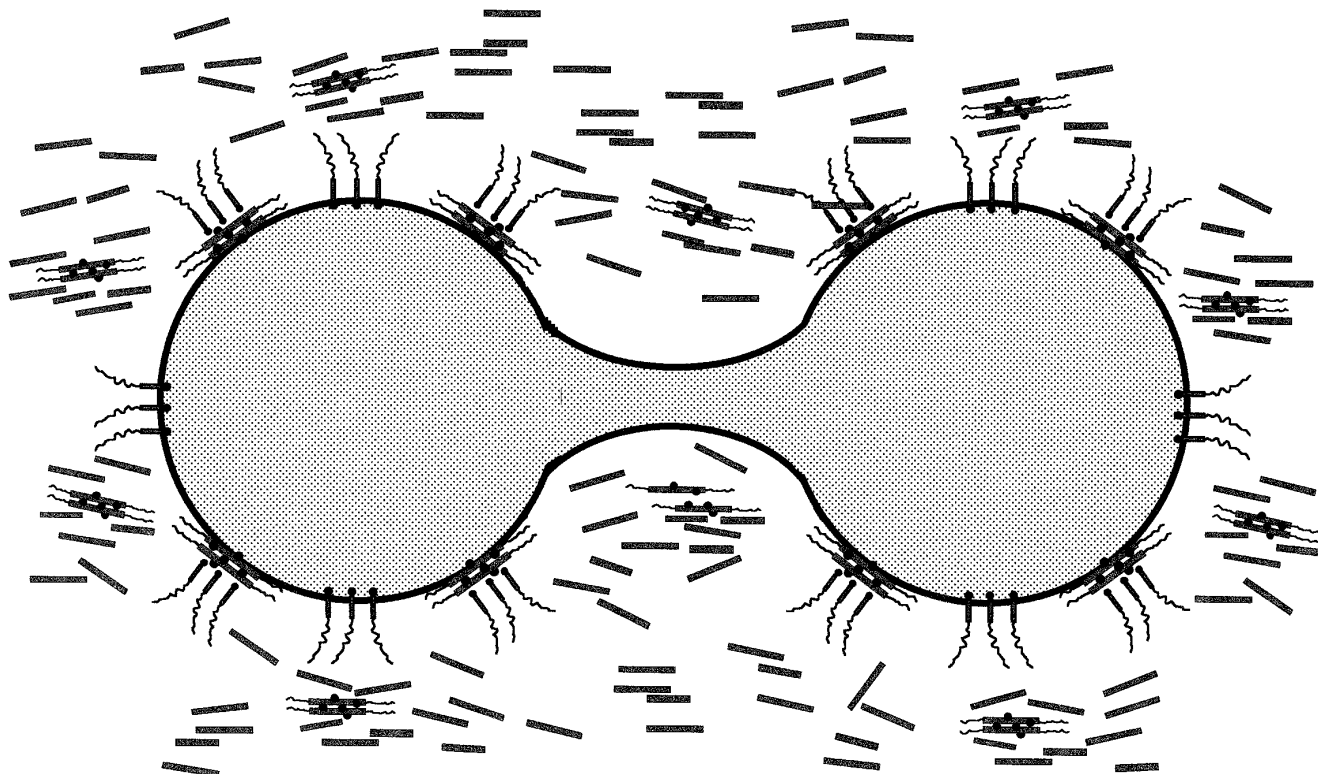


**FIG. 6.** Role of oil aromaticity on asphaltene state of aggregation and resulting interfacial activity: intermediate aromaticity (20-50% toluene-in-heptol). Note that droplets resist fusion due to steric stabilization.

While the emulsions produced from the model oils containing SJV asphaltenes were much more stable than those produced from the whole crude, the observed stability of the SJV model emulsions upon centrifugation were much more variable (i.e., less reproducible) than those of the other crudes. Some batches of SJV precipitated asphaltenes went into solution rather quickly while the material precipitated from other experimental runs was harder to dissolve or never went completely into solution. The batches of SJV asphaltenes that went into solution formed emulsions which were on the same order of stability as the ANS and AH model emulsions, while those that were more difficult to dissolve formed emulsions which were much less stable. The different batches of precipitated SJV asphaltenes must be characterized to determine the reason for this discrepancy in reproducibility. Until then, all the results concerning SJV asphaltenes presented in this work should be examined with this in mind.

As discussed previously, it is well known that resins are insufficient of themselves to stabilize emulsions to any considerable extent. True to form, none of the resin types from this study were able to form stable emulsions when dissolved in

the model oil. As pointed out by Mingyuan *et al.* (15), the instability of resin-stabilized emulsions is likely due to their smaller molecular size in comparison to asphaltenes. However, when the aliphatic content of the crude medium is increased to the point of precipitating the resins in the form of a fine dispersion, they should become more amenable to adsorbing and stabilizing the interface by forming a more rigid barrier to coalescence. Figure 2 shows this to be true in the case of SJV and AH resins where they were dissolved in pure heptane before emulsification. The emulsions formed from the heptane solution of AH resins were completely stable to gravity settling over a 24-h period, while SJV resins were only slightly less stable. The resins from ANS and AB were completely soluble (i.e., no observable precipitated solids) in pure heptane and were resolved soon ( $\sim 1$  min) after emulsification with water. (*Note.* All of these emulsions were completely resolved upon centrifugation at 5,000 rpm for 30 min.) This suggests that AH and SJV resins are more polar and/or aromatic than those from ANS and AB. Although this does not seem to be supported by the  $^{13}\text{C}$  NMR data and the detectable functional groups via FTIR (as presented in Table 1) concern-



**FIG. 7.** Role of oil aromaticity on asphaltene state of aggregation and resulting interfacial activity: high aromaticity (>50% toluene-in-heptol). Note that droplets fuse due to increased solubility of asphaltenes in mono- or dimolecular form and consequently desorb from interface.

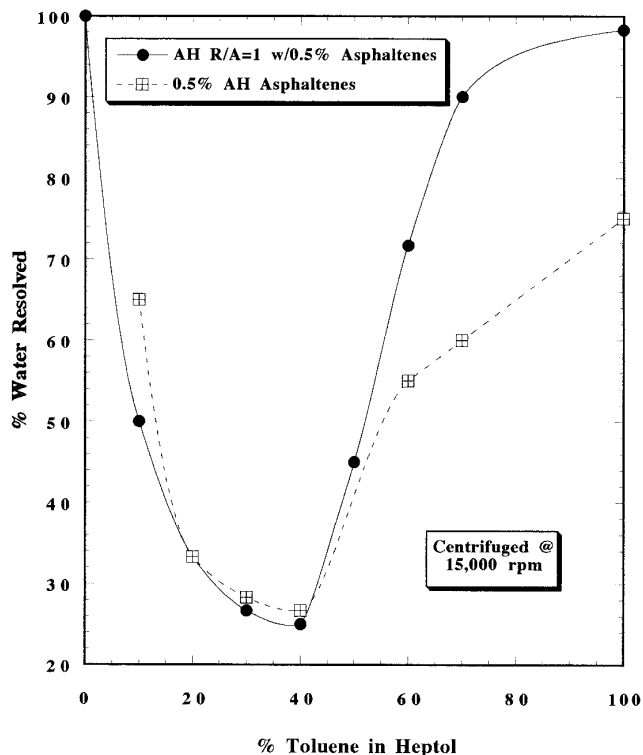
ing AH resins, the results from the integration of the FTIR aromatic carbon peak ( $\sim 1600\text{ cm}^{-1}$ ) do indicate this to be true for both AH and SJV resins. The *apparent* aromatic carbon concentrations of AH and SJV resins are 18.4 and 17.0%, respectively, while those of ANS and AB are only 11.9 and 11.7%. As discussed in our previous characterization study (14), the intensity of this peak is known to increase as a function of both the aromatic carbon content and the polarity of any neighboring functional groups.

*Effects of crude medium aromaticity.* To begin our investigation of the primary contributors to emulsion stabilization using these model oils, we decided to study the effects of varying the aromaticity of the crude medium in oils with different types of asphaltenes *in the absence* of any solubilizing resins. The aromaticity of the crude medium, the heptane-toluene mixture, was increased simply by increasing the proportion of toluene in the mixture. The results shown in Figs. 3 and 4 reveal that (1) the crude aromaticity is definitely a primary factor in determining the stability of asphaltene-stabilized emulsions, (2) there is a range in the aromaticity of the crude medium for which an optimum stability is observed, and (3) the asphaltene type plays at least a secondary role in determining the resultant emulsion

stability. (The difference in centrifugal field strength between these figures should be noted.) All the model oils are destabilized considerably at the extremes in crude aromaticity (<20% and >50% toluene) and exhibit their greatest stabilities between 30–40% toluene in heptol.

These results can be understood in light of the solubility state of the asphaltenes. Anisimov *et al.* (16) have established that asphaltenes from Arabian and Venezuelan crude oils were in true solution (at a concentration of 0.1 wt%) when the toluene concentration in heptol was greater than 50% (v/v) using photon correlation spectroscopy (PCS). When the toluene concentration was reduced from 50% to 10%, the asphaltenes were colloiddally dispersed and were ultimately precipitated out of solution. Flocs of Arabian Heavy asphaltenes were  $\sim 0.5\ \mu\text{m}$  in size in a 35/65 toluene/heptane mixture.

Therefore, at crude aromaticities lower than 20% toluene, some of the asphaltenes are certainly precipitated out of solution in the form of aggregates which are too large to adsorb and remain at the interface in order to effect the optimum degree of stabilization. This state of crude solvency is depicted schematically in Fig. 5. In the middle range of crude aromaticity (30–40% toluene), the asphaltenes are



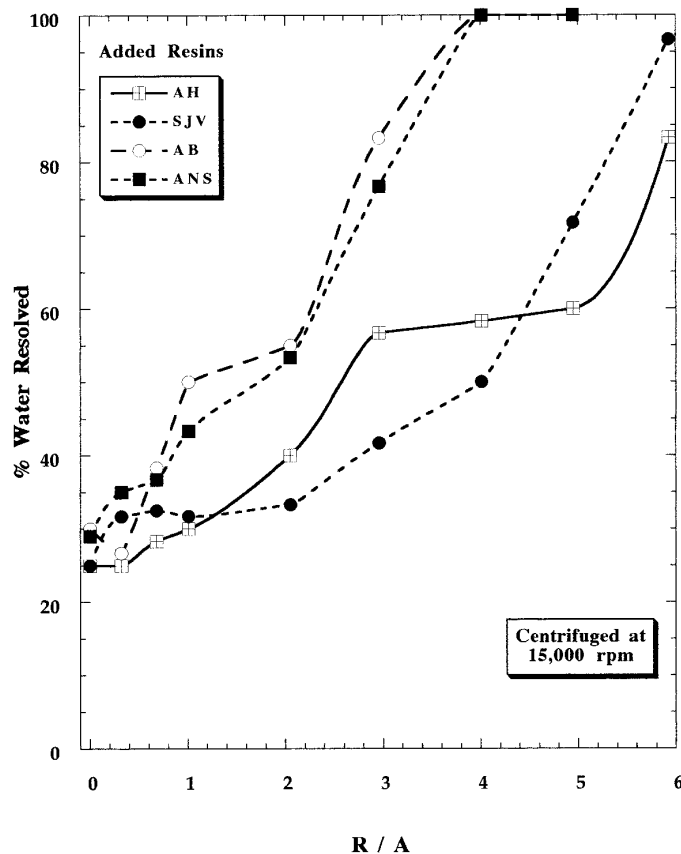
**FIG. 8.** Role of aromaticity (% toluene in heptol mixtures) on emulsion stability of 0.5 wt % AH asphaltenes in heptol mixed with water: comparison of pure asphaltenes with resins + asphaltenes ( $R/A = 1$ ).

most likely near or right at the point of precipitating in the form of a fine dispersion (i.e., very small particulates,  $1 \mu\text{m}$  OOM). Figure 6 shows this dispersion of fine asphaltene particulates to be capable of adsorbing and stabilizing the water-oil interface to the optimum extent by forming a barrier which is mechanically resistant to the coalescence of the droplet phase. At the upper end of the aromaticity spectrum, the asphaltenes are colloidal, if not molecularly, dissolved in the oil phase and are more content to remain there in place of becoming interfacially active. As shown in Fig. 7, emulsions produced from highly aromatic crude mediums are less stable to the coalescence and phase separation of the dispersed water droplets.

The results in Figs. 3 and 4 also show that AH, ANS, and SJV asphaltenes are very similar in their propensities to form stable emulsions in this optimum range of crude aromaticity. At aromaticities above 70% toluene, however, both the ANS and SJV asphaltene-stabilized emulsions are affected to a larger extent ( $\sim 15$ – $30\%$  additional water resolution) by crude solvency than the emulsions produced with AH asphaltenes. The SJV model emulsions are also much more destabilized at the lower extreme in crude aromaticities than AH. SJV and ANS asphaltenes are much more polar and/or aromatic than their AH counterparts as gauged by their polar

functional group and FTIR aromatic carbon content (see Table 1). This difference in polarity and aromaticity shows itself more at the extremes in crude aromaticity than it does in the optimum range of stability. This observation can be explained by recognizing that the lower and higher extremes of crude aromaticity likely result in a larger degree of aggregation and greater extent of solvation, respectively, with regard to the more polar, aromatic asphaltenes as one moves from the optimum state of stability.

Another experiment was conducted to discern the added dimension that the resins impart in determining the effect of the crude medium aromaticity on emulsion stability. Figure 8 shows the effect of varying the crude aromaticity in a model oil consisting of both AH resins and asphaltenes (0.5% Asp and  $R/A = 1$ ) and also compares these results with those of the model oil only containing 0.5% AH asphaltenes. First of all, the model oils containing both resins and asphaltenes exhibited the same trends in emulsion stability as previously observed for the asphaltene-only model oils. Both types of model emulsions were of similar stability in the middle range of crude aromaticity (20–50% toluene



**FIG. 9.** Effect of adding resins (varying  $R/A$ ) from different crudes on emulsion stability of 0.5 wt% AH asphaltenes in heptol (30% toluene, 70% n-heptane) mixed with water.

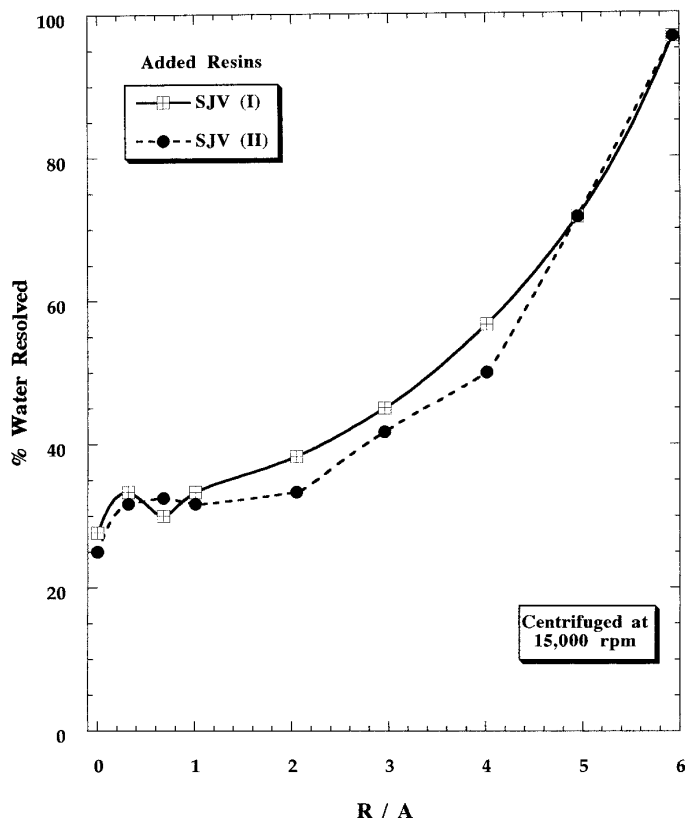


FIG. 10. Reproducibility of adding SJV resins (varying R/A) on emulsion stability of 0.5 wt% AH asphaltenes in heptol (30% toluene, 70% n-heptane) mixed with water.

ene in heptol); however, the asphaltene-only model oils were more stable at higher aromaticities and less stable in the lower extreme. The results at the extremes can be rationalized when bearing in mind that the resins help to solubilize the asphaltenes in both cases. At the higher extreme, the resins added to the dissolving power of the high crude aromaticity which caused the asphaltenes to go even more into solution and became less surface active. At the lower extreme, the resins still acted as solvating agents but served a different purpose. The resins shielded the asphaltenes from the increasingly aliphatic crude medium and restrained them from precipitating and forming the large agglomerates which are less effective in stabilizing emulsions. This effect is even more dramatic when considering the fact that the model oil containing both resins and asphaltenes in pure heptane formed an emulsion which was completely stable to gravity settling over a 24 h period before being resolved upon centrifugation. Of course, asphaltenes alone cannot dissolve in heptane (since they are, by definition, heptane-insoluble) and, therefore, are unable to form an emulsion. The similar stabilities observed in the middle range of crude aromaticities only suggest that the amount

of added resins are insufficient to impart any effect on the observed emulsion stability in this region.

*Effects of added resins and resin type.* The next logical step in the investigation was to determine the effect of increasing the amount of added resins (i.e., increasing the R/A ratio) at a constant asphaltene concentration and to investigate the effect of adding resins isolated from different crude types. Figure 9 shows the effect of adding resins from all four crude types on the stability of emulsions produced from model oils containing 0.5% AH asphaltenes. The first-order effect was that R/A ratios  $\geq 3$  did indeed diminish the emulsifying propensity of these model oils to a significant extent. These model emulsions were completely resolved (using the standard protocol) at an R/A = 4 with ANS and AB resins while AH and SJV resins required an R/A  $\geq 6$  to obtain the same resolution which also revealed the second-order effects of resin type on model emulsion stability. ANS and AB resins were more effective destabilizers than the resins isolated from SJV and AH. This is not surprising in light of the results from Fig. 2, where SJV and AH resins showed a greater ability to stabilize the water-oil interface in a model oil consisting of pure heptane.

Since the effects of resin type are not quite as evident as other variables we have studied, their reproducibility was tested, and a typical example is presented in Fig. 10. These results show the reproducibility of adding SJV resins to a model oil consisting of 0.5% AH asphaltenes to be very good. This is not only a reflection of the reproducibility of the formation and stability protocols, but also of the resinous and asphaltenic material obtained via fractionation from previous studies.

Figures 11 and 12 show the effects of adding these same resin types to model oils consisting of 0.5% ANS and SJV asphaltenes, respectively. The results from using ANS asphaltenes are very similar to those of AH asphaltenes in that ANS and AB resins again show themselves to be more effective in destabilizing the emulsions than their SJV and AH counterparts. With ANS asphaltenes, R/A values of 6 are not sufficient for AH and SJV resins to completely resolve the emulsions. This is different than that observed for AH asphaltenes, where complete resolution was attained at these values. It should also be noted that the stability observed for ANS resins and asphaltenes at an R/A = 3 ( $\sim 80\%$  water resolved) is very similar to the stability of an emulsion produced from ANS whole crude ( $\sim 70\%$  water resolved), which has an R/A = 2.8.

Also, there appears to be a slight stabilization in these model emulsions at an R/A = 0.33 for most of the resin types. This may be due to the breaking up of large asphaltene particulates from the initial asphaltene-only model oil upon addition of a small amount of resins. This would allow for more effective stabilization to the optimum state of asphaltene

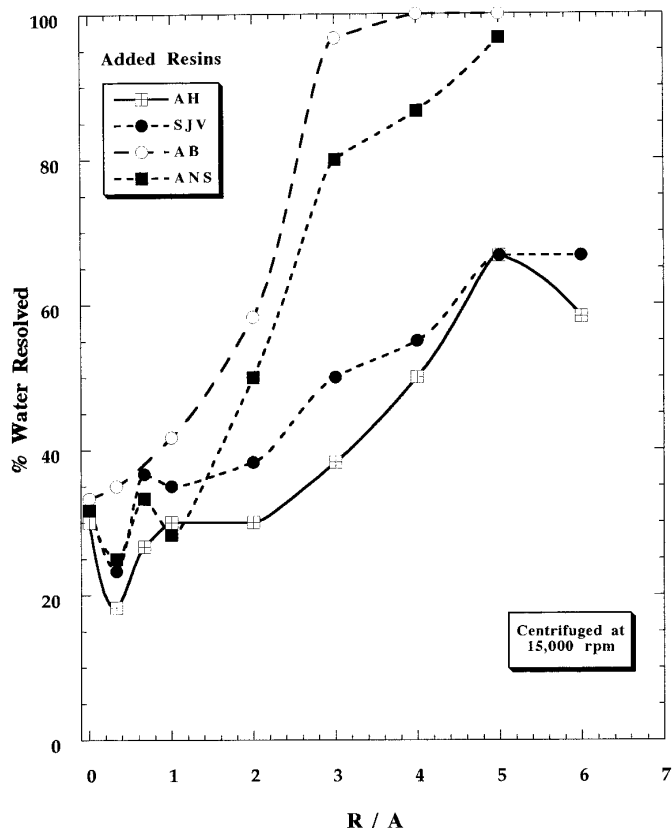


FIG. 11. Effect of adding resins (varying R/A) from different crudes on emulsion stability of 0.5 wt% ANS asphaltenes in heptol (30% toluene, 70% n-heptane) mixed with water.

solubility before subsequent addition of resins begin to further dissolve the asphaltenes and destabilize the emulsions. A similar phenomena has been reported by Mansurov *et al.* (17): a maximum in the shear strength of the interfacial film,  $\sigma_r$ , was observed at a 1:3 ratio of resins to asphaltenes for two different crude oils. This index serves as a measure of the tendency of asphaltenes to associate and is a direct characteristic of the stability of crude oil emulsions. Further increases in the relative amount of resins in the solution (i.e., R/A ratio) led to a decrease in the interfacial film strength.

With SJV asphaltenes (Fig. 12), the effects of resin type seem to be reversed from the results obtained when using AH and ANS asphaltenes (Figs. 9 and 11). These SJV asphaltenes are all from the same fractionation batch so they should be reproducible (as can be affirmed to some extent by the reproducibility of the 0% resin data points), but could not be tested given the insufficient amount of asphaltenes from this batch and the variability in results when using SJV asphaltenes from different batches. Keeping this in mind, SJV and AH resins are the most effective, respectively, in destabilizing emulsions produced from SJV asphaltenes at least for R/A's  $\leq 3$ . This

destabilizing effect is very "immediate" (i.e., at R/As  $\leq 1$ ) for these resins, especially when compared to the results from the other types of resins and even other asphaltene types (Figs. 9 and 11). Referring to Table 1, SJV asphaltenes are the most polar of the asphaltene types in this study. Asphaltenes which are very polar would likely require resins which are similar in nature to dissolve them effectively and destabilize the emulsions. SJV and AH resins are the most polar resin types, as discerned from the FTIR and metals analysis results, respectively. AB and ANS resins are much less effective as destabilizers when SJV asphaltenes are used. In fact, ANS resins are seemingly only effective enough to reduce the size of the asphaltene precipitates to the point that they actually help to stabilize the resultant emulsions at R/As  $\geq 3$ . At R/As  $\geq 3$ , AH resins appear unable to destabilize the model emulsions to any further extent, while AB and ANS resins finally show dramatic strides in lessening the emulsifying propensities of these oils.

All these effects concerning crude aromaticity and different amounts and functional types of resins and asphaltenes on the solvency and surface-active state of asphaltenes are brought

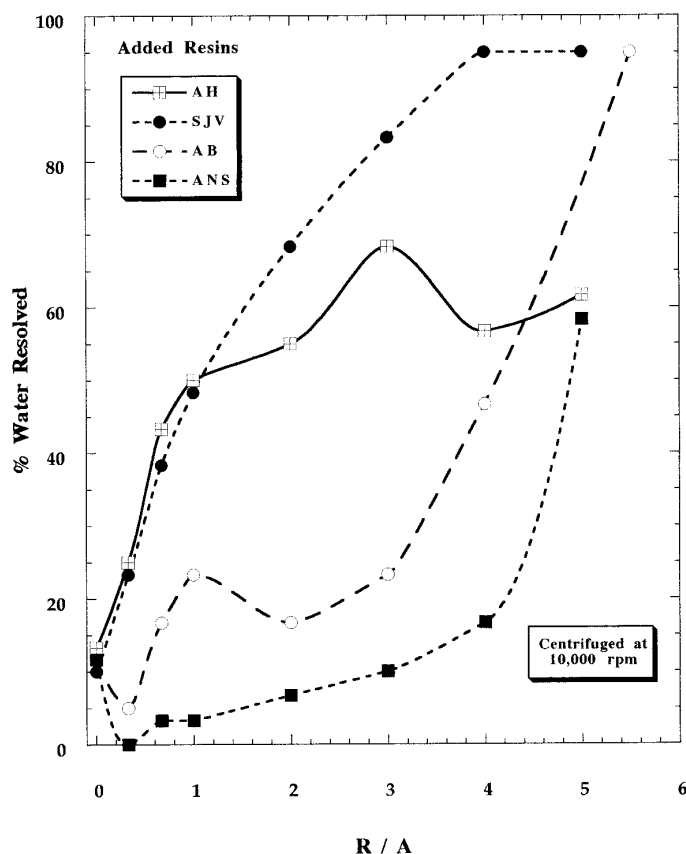


FIG. 12. Effect of adding resins (varying R/A) from different crudes on emulsion stability of 0.5 wt% SJV asphaltenes in heptol (30% toluene, 70% n-heptane) mixed with water.

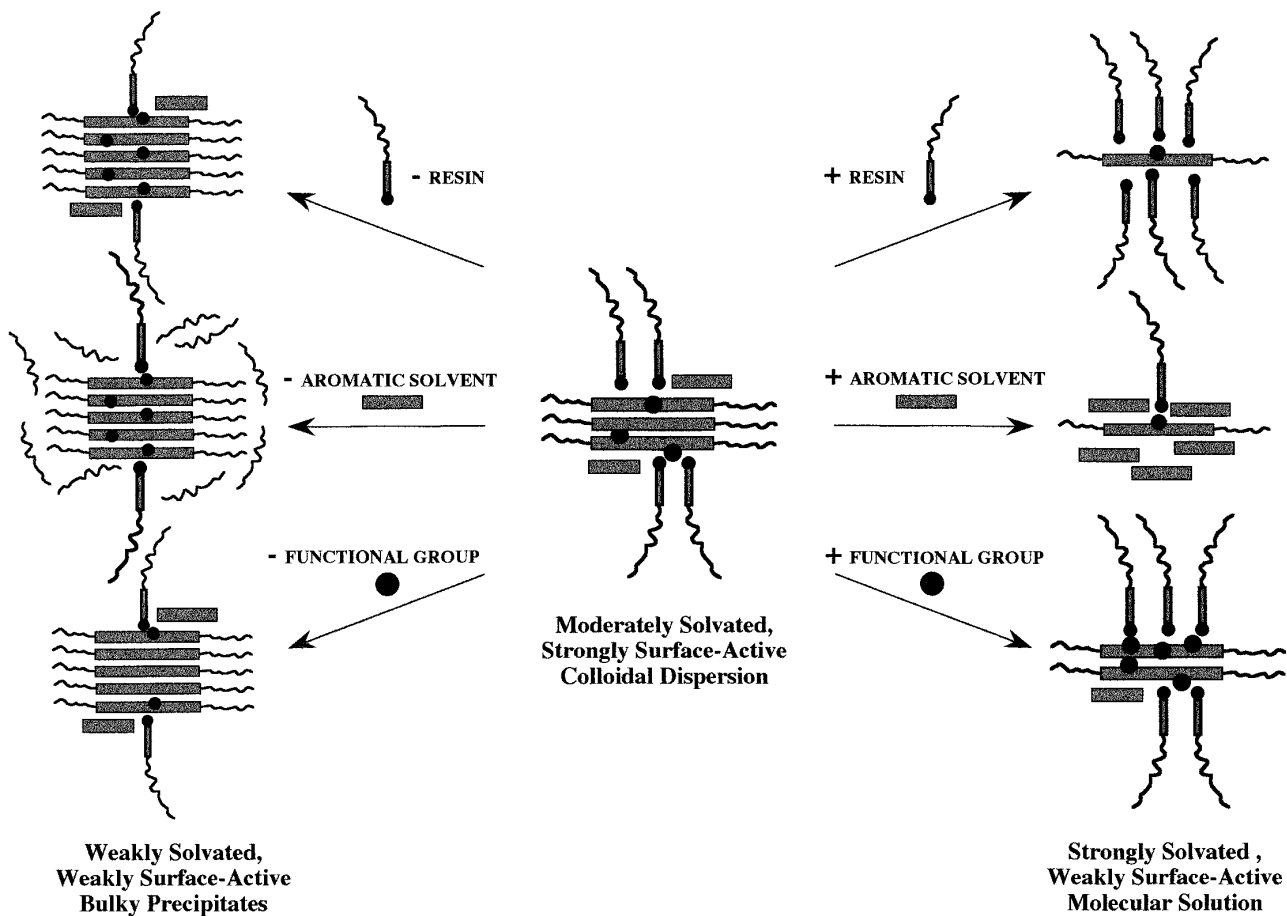


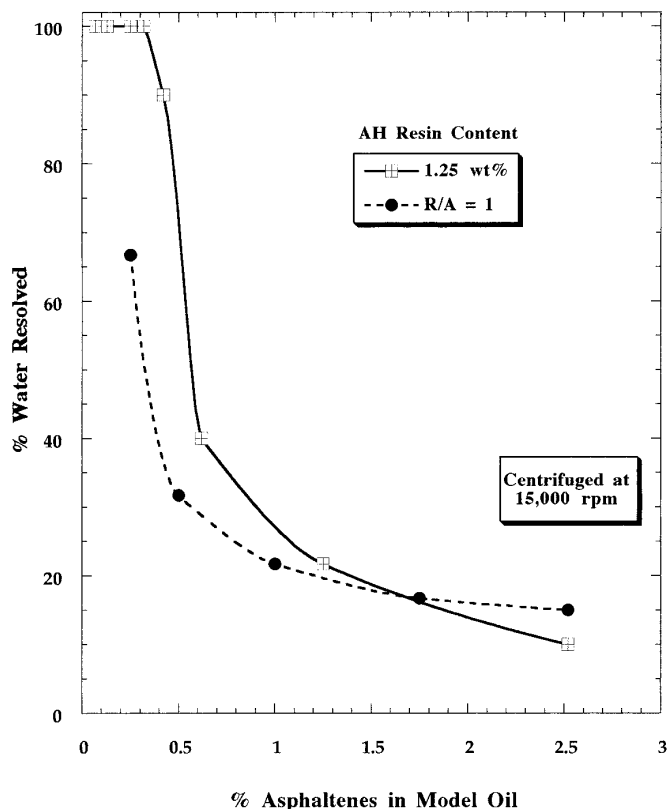
FIG. 13. Dominant contributors to asphaltene solubility, state of aggregation, and the resulting impact on interfacial activity.

together in a schematic illustration in Fig. 13. This figure shows the influence of any perturbations from the "ideal" solvency state (which results in the optimum emulsion stability), where the asphaltenes are colloiddally dispersed in the form of finely precipitated aggregates. Any change in crude aromaticity, R/A ratio, and/or polar functionality results in a destabilization of the produced emulsion. A decrease in any of these characterization parameters (or combination thereof) results in further precipitation of the asphaltenes into aggregates which grow too large to effectively adsorb and stabilize the interface, while an increase in solvency through these same channels provides an environment where the asphaltenes are more content to remain in the oil phase and thus considerably lowers their interfacial activity.

*Effects of asphaltene concentration.* The concentration of asphaltenes in the oil should also have a substantial effect on the emulsion stability. The results in Fig. 14 where the concentration of asphaltenes was increased both at a constant resin concentration of 1.25% and at a constant R/A ratio of 1, do indeed prove this to be true. The emul-

sions in this study begin to exhibit stabilities similar to those observed from the whole crudes at an asphaltene concentration of 0.5%, which was the concentration used in all the previous experiments. The emulsion produced at the lowest asphaltene concentration of 0.07% was completely resolved after gravitation for 24 h. The emulsion produced from the next highest asphaltene concentration of 0.13% as well as all of the remaining samples were completely stable to gravity over the same time period. In comparing the two curves, the constant resin concentration curve shows more water resolution than the constant R/A curve at asphaltene concentrations < 1.25% which demonstrates the destabilizing effects of the resins in this region. At an asphaltene concentration of 2.5% (with R/As of 0.5 and 1), there was virtually no measurable difference in the observed stabilities. This was the highest concentration of asphaltenes which could be completely dissolved in the heptol (7/3) medium.

*Characterization of residual model emulsions and oils.* The interfacially active material from the portion of the



**FIG. 14.** Comparison of varying versus fixed R/A ratio on emulsion stability of AH asphaltenes with AH resins in heptol (30% toluene, 70% n-heptane) mixed with water: fixed resin content (1.25 wt%) versus R/A = 1.

model emulsion that was stable to centrifugation (i.e., the residual emulsion) was isolated from the material that remained in the creamed oil phase, and both of these materials were characterized by elemental and neutron activation analyses. Some of the residual samples did not provide enough material from the oil phase to be characterized, and any of the model emulsions where the majority (<50%) of the emulsion was resolved could not be characterized. Therefore, the results from only a few of the model samples are presented in Table 2. The H/C values reveal that the interfacially active materials from asphaltene-only oils as well as oils that contain both resins and asphaltenes were more condensed and/or aromatic than the material in the oil phase, as would be expected. The results for the heteroatomic and metals contents suggest that the material at the interface is also more polar than what remains dissolved in the oil phase. By comparing these results with the characterization results of the resins and asphaltenes in Table 1, we also discovered that the interfacially active material from the resin- or asphaltene-only stabilized emulsions is

comprised of the most polar and/or aromatic portion of the resin or asphaltene fractions.

## CONCLUSIONS

In this work, emulsions produced from model oils containing resins and asphaltenes (or even just asphaltenes) exhibited stabilities which are very similar or in some cases even greater than those produced from the whole crudes. Therefore, the presence of waxes and inorganic solids may contribute to the observed stability of whole crude oils but is not essential to stabilize emulsions. Emulsions from some types of crude oils (e.g., AH and SJV) can also be stabilized to a limited extent by resins alone when in the presence of a highly aliphatic medium. There is evidence from the characterization of these resin types that they are more polar and/or aromatic than AB and ANS resins, which are completely soluble in an aliphatic medium and show no propensity to stabilize emulsions by themselves.

The primary contributors to the stability of emulsions produced in this study were the aromaticity of the crude medium (heptol), the concentration of asphaltenes, and the availability of solvating resins in the oil (i.e., the R/A ratio). The optimum emulsion stability was attained in the 30–40% toluene-in-heptol range and in many cases when a small amount of resins (i.e., R/A = 0.33) was added to the model oil. This strongly supports the notion that asphaltenes are the most effective in stabilizing emulsions when they are at or near the point of precipitation. The emulsion stability was significantly enhanced at higher asphaltene concentrations and lower R/A values. An asphaltene concentration of ~0.5% was required to produce an emulsion which was as stable as those produced from the whole crudes. The types of resins and asphaltenes used in constructing these oils and the synergy between these compounds appear to play a more secondary yet still very meaningful role in determining the resultant emulsion stability. For example, the polar resins isolated from SJV and AH were the least effective in destabilizing model emulsions produced from AH and ANS asphaltenes, but were found to be the most effective in destabilizing those produced from the more polar SJV asphaltenes. Also, characterization of the residual emulsion phase revealed that this interfacially active material was more polar and/or aromatic than the components remaining in the oil phase. These results reinforce the findings from our previous study on the emulsion stability of whole crudes and corroborate the proposed mechanism in which the solubility state of the asphaltenes is a critical factor in determining the extent to which these emulsions are stabilized.

Of course, there is much more to be done in this promising area of research. By using resins and asphaltenes isolated from other crudes to broaden the scope of this study and employing ion exchange separations to provide more defined

**TABLE 2**  
**Characterization of Residual Model Emulsion and Oil Phases**

Figure #	Model oil	Asp & res type & content	Phase	H/C	%N	%S	V (ppm)	Ni (ppm)
1	Heptol (7/3)	0.5% AH Asp	Emulsion	1.08	0.93	7.21	619.8	430.9
1	Heptol (7/3)	0.5% AH Asp	Oil	1.20	1.01	6.72	520.4	329.9
1	Heptol (7/3)	0.5% SJV Asp	Emulsion	1.10	2.57	1.98	609.3	2226
1	Heptol (7/3)	0.5% SJV Asp	Oil	1.24	2.38	1.89	326.8	521.9
1	Heptol (7/3)	0.5% AB Asp	Emulsion	0.95	0.80	5.28	351.7	16.2
1	Heptol (7/3)	0.5% ANS Asp	Emulsion	1.06	1.02	3.01	424.8	370.3
2	Heptane	0.5% AH Res	Emulsion	1.31	0.89	5.22	228.5	826.3
6	Heptol (7/3)	0.5% AH Asp	Emulsion	1.21	1.19	6.51	420.6	276.0
		1.0% AH Res						
6	Heptol (7/3)	1.0% AH Res	Oil	1.30	0.47	6.19	306.1	165.3
10	Heptol (7/3)	2.5% AH Asp	Emulsion	1.16	0.97	6.85	560.8	293.2
		1.25% AH Res						
9	Heptol (7/3)	0.5% SJV Asp	Emulsion	1.23	1.90	2.90	388.0	611.9
		0.5% AH Res						
9	Heptol (7/3)	0.5% AH Res	Oil	1.37	1.05	3.47	265.1	317.6
9	Heptol (7/3)	0.5% AH Res	Oil	1.37	1.05	3.47	265.1	317.6
9	Heptol (7/3)	0.5% SJV Asp	Emulsion	1.20	2.22	2.29	438.3	631.7
		0.5% ANS Res						
9	Heptol (7/3)	0.5% SJV Asp	Emulsion	1.31	1.55	2.84	235.3	415.0
		2.0% ANS Res						
9	Heptol (7/3)	2.0% ANS Res	Oil	1.36	1.42	2.64	185.0	263.0
9	Heptol (7/3)	0.5% SJV Asp	Emulsion	1.17	2.17	2.39	431.0	693.4
		0.5% AB Res						
9	Heptol (7/3)	0.5% SJV Asp	Emulsion	1.18	2.21	2.42	476.1	663.2
		0.33% AB Res						
9	Heptol (7/3)	0.33% AB Res	Oil	1.37	1.24	3.21	187.1	256.4

fractions, we will be able to investigate in further detail the role of these polar components and the mechanisms by which they stabilize crude oil emulsions.

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### REFERENCES

- McLean, J. D., and Kilpatrick, P. K., *J. Colloid Interface Sci.* **189**, 242 (1997).
- Waarden, M. v. d., *Kolloid Z. Z. Polym.* **156**(2), 116 (1958).
- Neumann, H.-J., *Petrochemie* **18**, 776 (1965).
- Eley, D. D., Hey, M. J., and Symonds, J. D., *Colloids Surf.* **32**, 87 (1988).
- Swanson, J. M., *J. Phys. Chem.* **46**, 141 (1942).
- Moschopedis, S. E., and Speight, J. G., *Fuel* **55**, 187 (1976).
- Burke, N. E., Hobbs, R. E., and Kashou, S. F., *J. Pet. Technol.* 1440 (1990).
- Yen, T. F., *Fuel Sci. Technol. Int.* **10**(4-6), 723 (1992).
- Al-Jarrah, M. M. H., and Al-Dujaili, A. H., *Fuel Sci. Technol. Int.* **7**(1), 69 (1989).
- Reynolds, J. G., and Biggs, W. R., *Fuel Sci. Technol. Int.* **4**(6), 749 (1986).
- Nghiem, L. X., *et al.*, *Soc. Pet. Eng.* **5**, 375 (1993).
- Tissot, B. P., and Welte, D. H., "Petroleum Formation and Occurrence: A New Approach to Oil and Gas Exploration," p. 527. Springer-Verlag, Berlin, 1984.
- Wiehe, I. A., *Fuel Sci. Technol. Int.* **14**,(1 and 2), 289 (1996).
- McLean, J. D., and Kilpatrick, P. K., *Energy Fuels*, **11**, 570 (1997).
- Mingyuan, L., Christy, A., and Sjoblom, J., in "Emulsions—A Fundamental and Practical Approach" (J. Sjoblom, Ed.), p. 157. Kluwer Academic, Dordrech/Norwell, MA, 1992.
- Anisimov, M. A., *et al.*, *J. Phys. Chem.* **99**, 9576 (1995).
- Mansurov, I. R., Il'yasova, E. Z., and Vygovskoi, V. P., *Chem. Technol. Fuels Oils* **23**(1-2), 96 (1987).