

Dynamic Asphaltene–Resin Exchange at the Oil/Water Interface: Time-Dependent W/O Emulsion Stability for Asphaltene/Resin Model Oils[†]

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The critical electric field (CEF) technique was used to determine the time-dependent stability of water-in-oil emulsions in which asphaltenes stabilize the film. Stabilizing films comprising purely asphaltenes were observed to increase monotonically in stability with time. However, in the presence of resins, particularly in mass ratios of resins to asphaltenes of 0.5–1.0, the stability of the emulsions as probed by CEF were observed to exhibit a very sharp local maximum. Similar behavior was observed in dilatational interfacial rheology experiments using an oscillating drop tensiometer. The dilatational modulus (ϵ) for the stabilizing film, as obtained from the variation of interfacial tension with interfacial area, of an aging asphaltene/resin model oil droplet in water exhibited a time-dependent local maximum. Values of ϵ were nominally lower for asphaltene/resin model oil systems than asphaltene model oil systems, qualitatively similar to CEF trends. These observed phenomena are similar to the “Vroman effect”, observed in competitive protein adsorption. One plausible explanation is that resin-solvated asphaltenic aggregates are able to diffuse and adsorb to the interface more quickly than larger pure asphaltenic aggregates, but then a molecular rearrangement occurs in which resins become the primary adsorbent in the monolayer by reptation through the consolidated asphaltene network, displacing the asphaltenes and reducing the stability and the dilatational elasticity.

1. Introduction

Water-in-crude oil (W/O) emulsions continue to challenge the petroleum industry during crude oil production, transportation, and processing.^{1,2} Asphaltenes and resins have been well-known to play very important roles in stabilizing water-in-crude oil emulsions.^{3–10} They adsorb onto and accumulate at W/O interfaces to form elastic, mechanically strong films surrounding water droplets. Formation of an interfacial film possessing

certain surface-rheological properties is obviously of fundamental importance for the stability of crude oil emulsions.^{11,12} Many research groups have studied extensively this subject for decades.^{13–31} The results of both surface and interfacial film studies of asphaltenes or resins indicate that asphaltene films

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are elastic solids and relatively immobile and irreversibly adsorbed, while resin films are less dense and easily disrupted. However, resins are known to adsorb more strongly than asphaltenes, as evidenced by the lower interfacial tension that they impart to oil–water interfaces. Asphaltenic film properties are significantly influenced by the oil phase aromaticity, the concentration of asphaltenes, and aging time, whereas resin film properties are much less influenced by these factors.^{20,31} For mixed asphaltene/resin systems, the resin to asphaltene ratio (R/A), the aromaticity of the oil phase, and the aging time dictate the film properties.

Although surface and interfacial film phenomena occur on a molecular scale, most investigations of film properties were performed on a more macroscopic scale. For example, Langmuir–Blodgett and planar interfacial rheology studies are constrained to much lower total interfacial areas than actual emulsions. The complexity of the mixture that makes up crude oil, as well as the opacity of their emulsions makes measuring emulsion film properties *in situ* a difficult task. Additionally, the correlation of emulsion stability with a fundamental knowledge of the film formation is still far from completely understood.

Here, we use the critical electric field technique^{32–34} to investigate the stability of water in model oil emulsions in which mixtures of asphaltenes and resins stabilize the film. In the critical electric field technique, a W/O emulsion sample is placed between two electrodes with a well-defined gap width and the current across the gap is measured as the voltage is increased in a stepwise fashion. Increasing the voltage induces the water droplets to become polarized, which subsequently form chains of droplets spanning the gap between the electrodes. As the voltage increases, the electromotive force on ions within the droplets becomes sufficient to cause the ions to rupture the

stabilizing films and the current is observed to increase sharply. This observed electric field (in kilovolts per centimeter) is called the critical electric field (CEF). The emulsion stability as gauged by the critical electric field correlates with the properties of the interfacial films including the concentration of asphaltenes, resin-to-asphaltene ratio (R/A), and aging time.^{32,33}

Asphaltenic films at model oil/water interfaces have recently been investigated using a serrated-edge biconical bob interfacial shear stress rheometer.³⁵ The authors tracked film strength with frequency sweeps at 1 hr intervals to recover the elastic storage (G') and viscous loss (G'') moduli. In asphaltene-only systems, the interfacial shear elasticity (G') increased monotonically for hours-to-days due to a plentiful asphaltene supply. After replacing the asphaltene solution with fresh solvent, the elastic modulus increased for another 8 h; a result of the molecular rearrangement of asphaltenes at the interface that leads to a cross-linked network. Replacement of the asphaltene solution with a resin solution led to a rapid reduction in elasticity followed by a slow increase, presumably due to solvation of asphaltenes and their removal/replacement at the interface.

Interfacial dilatational rheology has proven to be a useful technique for probing the interfacial adsorption behavior of surfactants,^{36,37} proteins,³⁸ and mixed protein/surfactant systems³⁹ as well as the elasticity of protein films at air–liquid⁴⁰ and liquid–liquid⁴¹ interfaces. This technique has also been used to explore film elasticity for crude oil–water,^{42–44} model oil–water,^{45–48} and model oil–air⁴⁹ interfaces. In interfacial dilatational rheology of a liquid–liquid interface, a droplet is formed

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Table 1. Elemental Composition of A and B Asphaltenes and Resins

	A asphaltenes (AA)	B asphaltenes (BA)	A resins (AR)	B resins (BR)
H/C	1.19	1.24	1.44	1.51
C%	82.69	78.47	79.72	79.21
H%	8.21	8.09	9.55	9.95
N%	1.02	1.87	0.81	1.48
S%	8.32	6.68	6.35	6.91
O%	1.64	2.9	3.58	1.98

and the interfacial tension (γ) is tracked as a function of time. To recover rheological information about monolayers or third-phase films at the interface, controlled oscillatory strain deformations of interfacial area (A) are applied and the resulting stress, i.e., interfacial tension, is recorded. The interfacial dilatational modulus (ϵ) is defined by the following expression:⁴²

$$\epsilon = \frac{d\gamma}{d \ln A} \quad (1)$$

With small oscillatory deformations of area with frequency ω , the dilatational modulus can be expressed as a complex quantity, with elastic and viscous contributions:

$$\epsilon = \epsilon_d + i\omega\eta_d \quad (2)$$

where η_d is the dilatational viscous modulus and ϵ_d is the dilatational elastic modulus. Depending on the system of interest, the $\gamma(t)$ response may lag behind the imposed $A(t)$, and this lag is described by a phase shift, ϕ . Purely elastic interfaces exhibit $\gamma(t)$ behavior completely in-phase with $A(t)$, i.e., $\phi = 0$ rads, whereas purely viscous interfaces are completely out-of-phase, having $\phi = \pi/2$ rads. The elastic and viscous moduli can then be expressed as functions of the magnitude of the dilatational modulus, $|\epsilon| = (\epsilon_d^2 + \eta_d^2)^{1/2}$, and the phase shift can be expressed by the following:

$$\epsilon_d = |\epsilon| \cos \phi \quad (3)$$

$$\omega\eta_d = |\epsilon| \sin \phi \quad (4)$$

2. Experimental Details

2.1. Materials. Two asphaltene samples from Arab Heavy (A) and California offshore (B) crude oils were precipitated by mixing 40:1 (mL:g) of heptane:crude and stirring for 24 h. Asphaltenes were vacuum filtered using Whatman 934AH filter paper and then rinsed with boiling heptane using a Soxhlet apparatus. Asphaltenes were recovered from the Soxhlet using toluene and a Buchi EL131 rotary evaporator. The two resin fractions were obtained by sequential elution chromatography^{5,50} of the deasphalted crude (maltenes), which was previously adsorbed onto silica gel. To minimize oxidation, all samples were blanketed with Argon gas in sealed jars and stored in a desiccator cabinet. Properties of A and B asphaltenes and resins are listed in Table 1. As expected, the H/C ratios for the resins are close to 1.5, while only ~ 1.2 for the asphaltene fractions.

Toluene and *n*-heptane were HPLC grade and supplied by Fisher Scientific. The 50:50 (v/v) *n*-heptane:toluene mixture will be referred to as *heptol*. Deionized water with 1% (w/w) NaCl added was used for preparing emulsions. After NaCl addition, the aqueous phase pH was adjusted to 6 with dilute HCl and NaOH.

2.2. Water-in-Asphaltene Model Oil Emulsion Preparation. The required asphaltene amount was weighed and dissolved with 3.5 mL of toluene in a 10 mL vial with a cap. The asphaltene and

toluene solutions were shaken for 24 h, and 3.5 mL of *n*-heptane was subsequently added. This asphaltene in heptol mixture was shaken for 24 h, whereupon 3 mL water was added to the asphaltene solution and then was emulsified for 3 min at 15 000 rpm using a Virtis Cyclone IQ² Homogenizer equipped with a 6 mm homogenizer tip.

2.3. Water-in-Asphaltene/Resin Model Oil Emulsion Preparation. The required asphaltene mass was weighed and dissolved with 3.5 mL of toluene in a 10 mL vial. The required amount of resins was weighed and dissolved with 3.5 mL of *n*-heptane. The asphaltene/toluene solution and the resin/*n*-heptane solution were each shaken for 2 h, after which the two solutions were mixed and shaken for 24 h. After 24 h, 3 mL of water was added to the mixture and then emulsified for 3 min at 15 000 rpm.

2.4. Critical Electric Field Measurement. After emulsification, the samples were aged at room temperature up until the CEF measurement was performed. To measure CEF, an emulsion sample was syringed into the sample cell consisting of two, 1.0 cm diameter, gold-plated, copper electrodes, separated by Mylar spacers and held in an aluminum casing (cf. Figure 1). The cell was connected to a HP6634B power supply (0–100 V DC source), controlled by a PC through the use of an HP82350A interface card. The power supply was controlled using an internally coded Visual Basic program. The gap width, δ , of the cell could be varied using Mylar spacers, but for all of the experiments, it was maintained at 0.25 mm. After the cell was loaded with the sample, the voltage between the electrodes was increased in increments of 0.25 V every 5 s and the current was measured 2 s after every step change (to avoid current spikes). This procedure typically continued through an abrupt—although on occasion gradual—change in the slope of the current (I) vs voltage (V) plot until the instrument overcurrent protection was activated, ending the experiment. Defining the critical voltage is an important aspect of this work, with consistency being the most critical concern. Here, we define the critical voltage at the intersection that occurs between tangent lines of the two extreme slopes in the resulting I vs V plot. The CEF is then defined as this critical voltage divided by the gap width separating the electrodes. Consistent sampling of the emulsions was also of great importance such that the emulsions were always pipetted from a location 1 cm below the free surface after resuspending the settled/aged samples. Microscopic observations were performed on an Olympus BH-2 stereomicroscope in parallel with CEF measurements to verify valid sampling procedures. Each of the model oil systems appeared to have acceptable droplet size polydispersity (0.5–20 μm) to ensure valid comparisons from sample to sample. All experiments were performed at room temperature.

2.5. Dilatational Rheology. All dilatational rheology experiments were run on an oscillating pendant drop tensiometer (TRACKER) from IT Concept (now Teclis), for which a schematic is shown in Figure 2. This setup was equipped with (A) a halogen lamp light source, (B) a cuvette containing the model oil drop in water, and (C) a charge-coupled device (CCD) camera. A DC motor controlled the drop volume by adjusting the plunger position in (D) a microsyringe containing the model oil. Finer control of drop volume was afforded by using lower-capacity microsyringes (250 μL) and higher-gauge (≥ 20) curved needles. A personal computer (D) analyzes images of the droplet shape to solve for γ from the force balance between Laplace and head pressure on the droplet.

Samples of B asphaltenes were prepared in 1:1 (v:v) blends of toluene and *n*-heptane and were run at 2% (w/w) with a 5 μL drop volume and 0.5 μL oscillations. Mixtures of B asphaltenes and resins were prepared with R/A = 0.5 and asphaltene compositions of 2% and 4% (w/w). A sample of 1% resin-only solution in the same solvent was also prepared and run on the TRACKER. The aqueous bulk phase was adjusted to pH 6 with dilute NaOH and HCl. Volume oscillations were induced with a frequency of 0.1 Hz for 10 cycles at each time point. These oscillations were typically performed every 10–15 min for the first hour of aging and then every 2 h thereafter. A single drop was used throughout the entirety of a run, which generally consisted of 15–20 time point measurements. This was done in order to ensure that time-dependent

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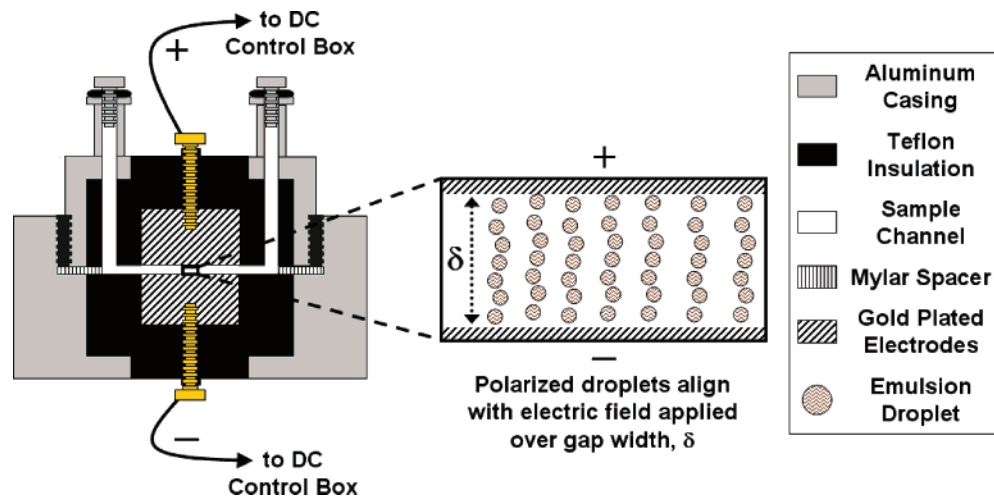


Figure 1. CEF sample cell with a two-piece aluminum housing that screws together closing down on Mylar spacers of known thickness. This enables tuning of the separation gap distance, δ , between the two gold plated electrodes. The expanded portion of the diagram illustrates the aligning of water-in-oil emulsion droplets with the applied electric field.

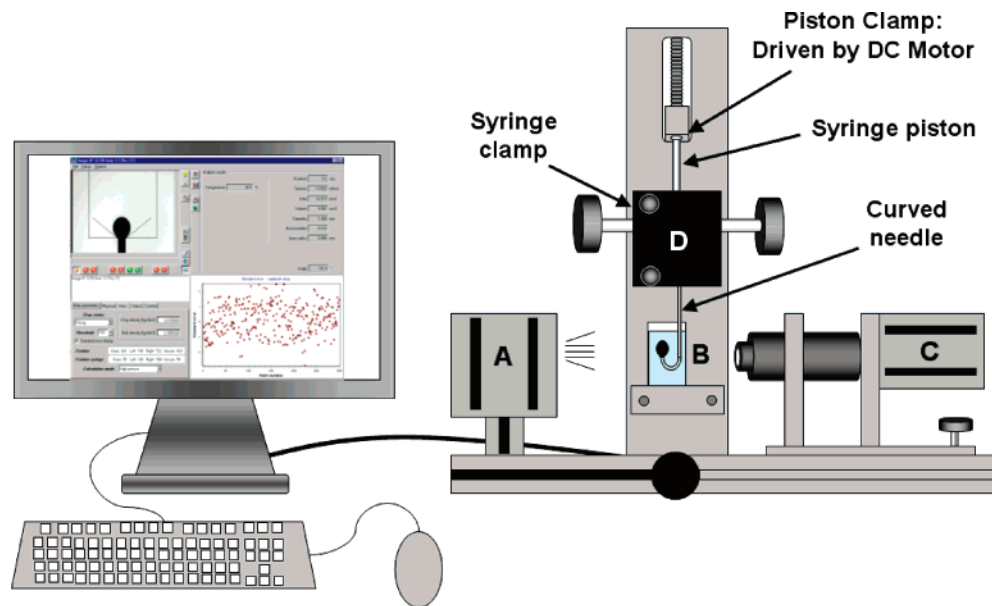


Figure 2. TRACKER instrument with (A) a halogen lamp, (B) a glass cuvette in which a droplet is oscillated, (C) a CCD camera, (D) a microsyringe containing the model oil, and (E) a personal computer to analyze the drop shape.

observations for a sample were not influenced by drop-to-drop variations that can occur. Total run times were generally 15–30 h. The DROP control/data analysis program was used to smooth the area and tension oscillations and calculate the dilatational modulus ($|\epsilon|$) and phase shift (ϕ). For both parameters, $|\epsilon|$ and ϕ , the values presented are from averaging over the 10 oscillation cycles applied at each time point.

3. Results and Discussion

3.1. CEF of Water-in-Asphaltene Model Oil Emulsions as a Function of Time. In order to assess emulsion stability kinetics, separate emulsions were prepared using B asphaltene in model oil and each emulsion was aged separately prior to the CEF measurement corresponding to the appropriate aging time (cf. Figure 3). It is clear that the CEF, i.e., emulsion stability, of these emulsions is a very strong function of adsorption/aging time. For B asphaltene concentrations below 1 wt %, the CEF increases monotonically for the first 6 h. After about 1 d of aging, emulsions made with 0.5% or 1% B

asphaltenes exhibited similar stability (~ 0.8 kV/cm). Emulsions prepared with 2% and 4% B asphaltene model oil approached their long-time (≥ 24 h) stability within the first few hours, at CEF values of about 1.2 and 2.8 kV/cm, respectively. These results indicate that, for model oils of low asphaltene composition, the interfacial asphaltene concentration is too small to dictate emulsion stability immediately after emulsification. Given enough time, however, asphaltenic aggregates will continue diffuse to the W/O interface and accumulate with ample material to cover the droplet surface and rearrange into an elastic film. Alternatively, in emulsions prepared with concentrated asphaltene model oils, the driving force for asphaltene adsorption at the W/O interface from the oil phase is significantly greater than that of less concentrated asphaltene solutions. Thus, at short aging times, the interfacially active asphaltene inventory in the continuous phase is plentiful, enabling adsorption to, and saturation of, the W/O interface, providing a barrier to coalescence rather quickly. Therefore, further extending the adsorption

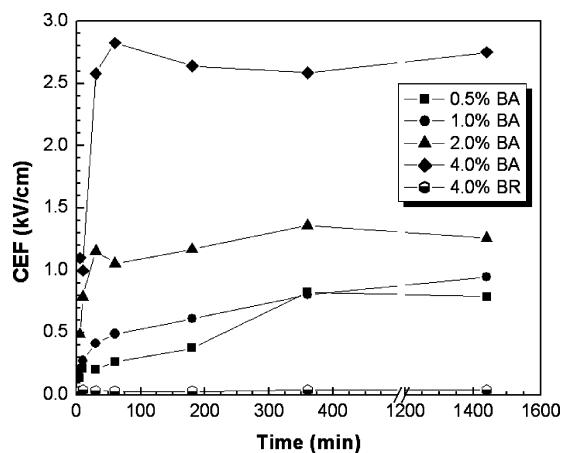


Figure 3. CEF for four different B asphaltenes (BA) model oil emulsions (0.5–4 wt % BA) as a function of time (0–1600 min) and one B resins (BR) model oil emulsion prepared at 4 wt % BR. A break in the time axis is made, omitting the 500–1200 min range during which no CEF data was collected.

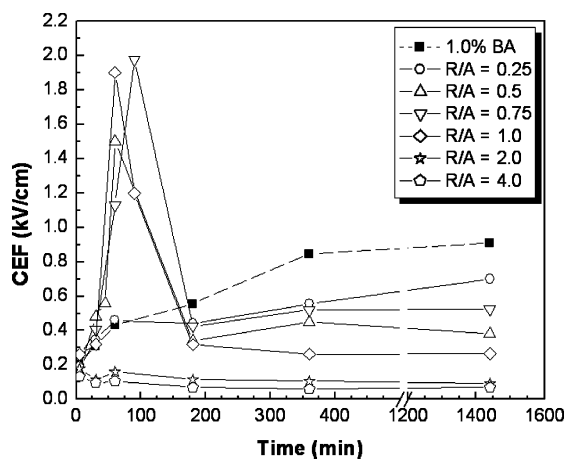


Figure 4. CEF for six different model oil emulsions made with B asphaltenes (BA) and B resins (BR) as a function of time (0–1600 min). All BA/BR model oils mixtures were prepared with 1 wt % BA and resin-to-asphaltene ratios (R/A) of 0.25–4. Also presented here is the base case of 1 wt % BA. A break in the time axis is made, omitting the 500–1200 min range during which no CEF data was collected.

time for concentrated asphaltene-only systems has little influence on the overall emulsion stability.

Also presented in Figure 3 is the CEF for a 4% resin-only model oil emulsion as a function of aging time. We can clearly observe the weak emulsion stabilizing power of this concentrated solution of resins. Resins are thought to be more surfactant-like than asphaltenes and form a monolayer as opposed to the multilayered and crosslinked film that has been reported for asphaltenes. This should be evident in the discussion of interfacial rheology of resin-only systems that is found later in this text.

3.2. CEF of Asphaltene/Resin Model Oil Emulsions as a Function of Time. Shown in Figures 4 and 5 is the time-dependent emulsion stability for emulsions made with model oils containing both asphaltenes and resins from crude B or A. For the mixed B asphaltene (BA) and B resin (BR) emulsions, we observed local maxima in the CEF profile within 50–90 min when R/A is between 0.5 and 1. When R/A = 1, the observed CEF passed through a maximum ca. 1.9 kV/cm at adsorption times of ~90 min, while after further aging (several hours), the CEF returned to <1.0 kV/cm. A similar local maximum also was observed in time-dependent CEF measure-

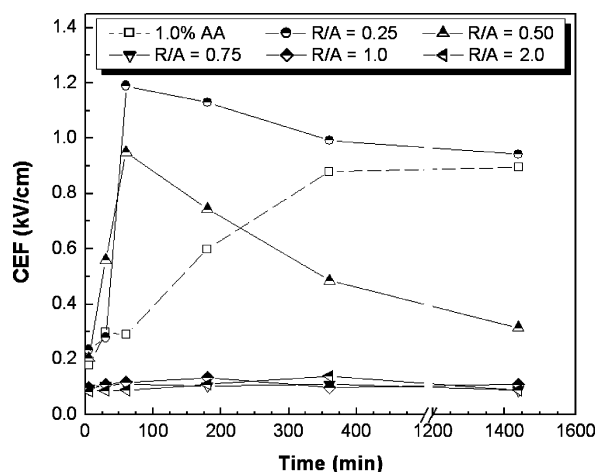


Figure 5. CEF for six different model oil emulsions made with A asphaltenes (AA) and A resins (AR) as a function of time (0–1600 min). All AA/AR model oils mixtures were prepared with 1 wt % AA and resin-to-asphaltene ratios (R/A) of 0.25–2. Also presented here is the base case of 1 wt % AA. A break in the time axis is made, omitting the 500–1200 min range during which no CEF data was collected.

ments of A asphaltenes/A resins model oil emulsions when R/A was 0.25–0.5. In Figure 4, we observe for R/A = 0.25 that this maximum of 1.2 kV/cm occurs after nearly 50–60 min after emulsification, while the CEF then decreased to 0.96 kV/cm after 24 h.

We should note that this behavior is not unique to these asphaltene/resin systems. In fact, this phenomenon bears strong resemblance to multiprotein adsorption commonly observed in biomaterials. In such systems, the adsorption of one protein increases with time, attains a peak value, and then partially or completely desorbs or is replaced by other proteins. This results from a dynamic exchange of proteins in the adsorbed protein layer. Proteins may replace each other in a well-defined order before the steady-state composition of adsorbate is reached, and this phenomenon is now called the Vroman effect.^{51,52} Both asphaltenes and resins exhibit significant molecular size polydispersity and chemical heterogeneity. Resins can exhibit the ability to solvate “pure” asphaltenes, possibly by disrupting the π - π overlapping prevalent within asphaltenic aggregates.⁵³ The maximum CEF value of asphaltene/resin model oil emulsions occurs at short times, which indicates very stable emulsions and, presumably, higher ordered self-assembled asphaltenic films, which diminish over time in either film composition or film elasticity per unit mass. In this regard, we believe resins may change the soluble state of asphaltenes, enhancing their interfacial activity and self-assembly upon a fresh interface. At longer times, however, thermodynamics favor resin adsorption to the interface to minimize the surface free energy. Resins modulate the asphaltenic film and either “loosen” the asphaltenic crosslinks at the interface (reduction in elasticity per unit mass) or “dissolve” the asphaltenes and displace them from the interface (reduction in interfacial concentration). Such interfacial denaturing would result in the time-dependent emulsion stability observed in our experiments.

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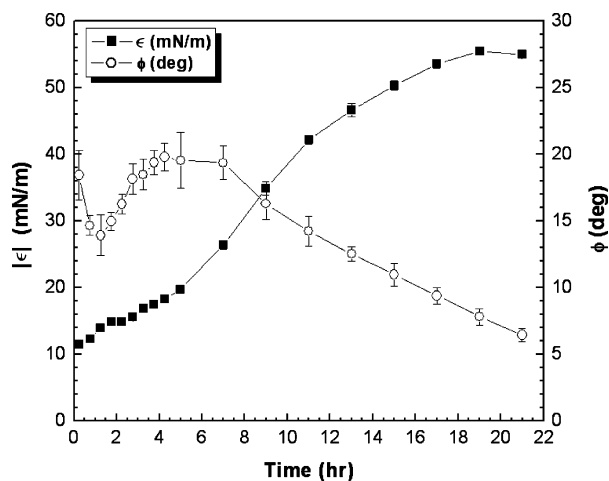


Figure 6. Dilatational modulus and phase angle for 2% B asphaltenes in 50:50 heptol in pH 6 deionized water. $V_{\text{drop}} \sim 5 \mu\text{L}$, $V_{\text{osc}} \sim 0.5 \mu\text{L}$, $\omega = 0.1 \text{ hz}$, and $T \sim 30 \text{ }^\circ\text{C}$. Note the decreasing phase angle with an increasing modulus, indicative of an increasingly elastic contribution to the total modulus.

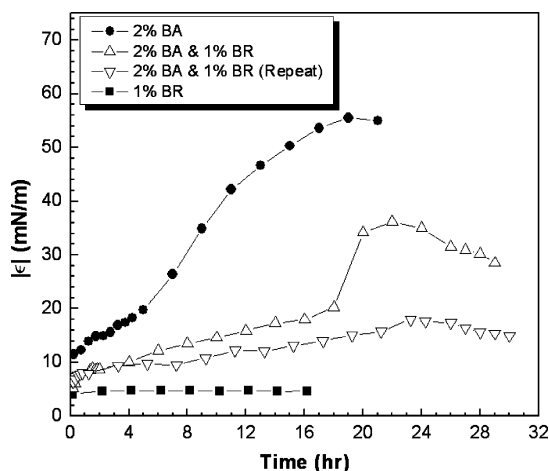


Figure 7. Dilatational modulus for two runs of 2% B asphaltenes (BA) and 1% B resins (BR) in a 50:50 heptol mixture in pH 6 deionized water. $V_{\text{drop}} \sim 5 \mu\text{L}$, $V_{\text{osc}} \sim 0.5 \mu\text{L}$, $\omega = 0.1 \text{ hz}$, and $T \sim 30 \text{ }^\circ\text{C}$. Also presented are the dilatational moduli for the BA-only and BR-only in 50:50 heptol drops in pH 6 deionized water.

3.3. Dilatational Rheology. Presented in Figure 6 are the time-dependent dilatational modulus and phase shift for a 2% B asphaltene model oil droplet. Not only does the dilatational modulus increase with time, but the phase shift also decreases, indicating that the contribution to the modulus is becoming increasingly elastic. This B asphaltenic film approaches an apparent equilibrium elasticity near 55 mN/m after roughly 20 h of aging. Asphaltenic films prepared at the cyclohexane/water interface have demonstrated similar aging dependence for asphaltene-only systems.⁴⁸

For asphaltene/resin mixtures at an R/A of 0.5 and a 2% B asphaltene concentration, the dilatational modulus was well below that for asphaltenes alone but well above the resin-only curve as seen in Figure 7. Two runs were performed for this mixed asphaltene/resin condition to test repeatability. After 18–23 h of aging there was an increase in the dilatational modulus for the asphaltene/resin mixtures followed by a gradual decrease for each run. However, there is a discrepancy between the two runs regarding this sudden increase in elasticity. Dilatational rheology reproducibility issues in asphaltene/resin systems have been previously reported,⁴⁹ which serves as a reminder of the

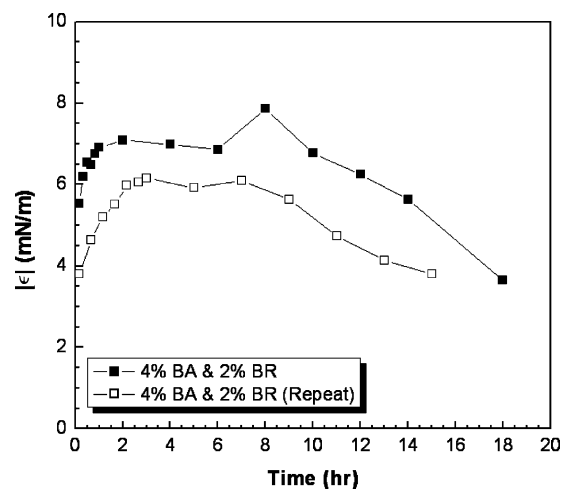


Figure 8. Dilatational modulus for two runs of 4% B asphaltenes (BA) and 2% B resins (BR) in 50:50 heptol in pH 6 deionized water. $V_{\text{drop}} \sim 5 \mu\text{L}$, $V_{\text{osc}} \sim 0.5 \mu\text{L}$, $T \sim 30 \text{ }^\circ\text{C}$. Although not quantitatively reproducible, the maximum in dilatational modulus as a function of time is qualitatively repeatable.

chemical heterogeneity and size polydispersity inherent in asphaltenes and resins that likely lead to the observed variability here.

For the resin-only system in Figure 7 the low dilatational modulus indicates a weakly elastic adsorbed layer. It should be noted, however, that, despite this low elasticity, the resin adsorption led to an interfacial tension of $\sim 6.5 \text{ mN/m}$. This is indicative of a high affinity for the interface by B resins, more so than that of B asphaltenes, which only reduced the tension to $\sim 18 \text{ mN/m}$. It is important to remember that, in this technique, we are testing the ability of the interface to respond to the interfacial deformation and the resulting changes in interfacial tension. A likely source for the elasticity in the resin-only system is either the Gibbs–Marangoni effect³⁷ or diffusion exchange⁴⁵ between the bulk and the interface during oscillatory droplet deformation, rather than the formation of a mechanically elastic network. It is likely then that resins form an interfacial structure comparable to a monolayer, rather than a crosslinked network, which presumably dictates resin interfacial behavior in mixed asphaltene/resin systems. Recall that resin-only emulsions showed little or no stability under the conditions tested, which may be related to the observed low dilatational modulus.

Although the results in Figure 7 exhibit a time-dependent maximum in film strength, we acknowledge its occurrence at much longer aging times than those observed in the emulsion. However, the diffusion length scales likely differ greatly for asphaltenes in the continuous phase of an emulsion and in the droplet of the tensiometer. In an effort to reduce the time needed to reach the maximum film strength, we performed two runs for mixtures of 4% B asphaltenes and 2% B resins as shown in Figure 8. While there is a noticeable quantitative discrepancy between the two data sets, the dilatational modulus qualitatively behaves quite reproducibly as a function of time. In both runs, a local maximum occurs within the first 4 h, but neither reaches the maximum elasticity observed for the 2% B asphaltene-only or 2% B asphaltene/1% B resin systems. The increased asphaltene concentration would have enhanced the inventory capable of migrating to the interface, which would normally yield an increase in film strength. However, we also increased the inventory of resins, which have a higher affinity for the interface than asphaltenes. We postulate that the resins displace asphaltenes from the interface, but only after repeating through the consolidated asphaltenic film, as drawn in the schematic in

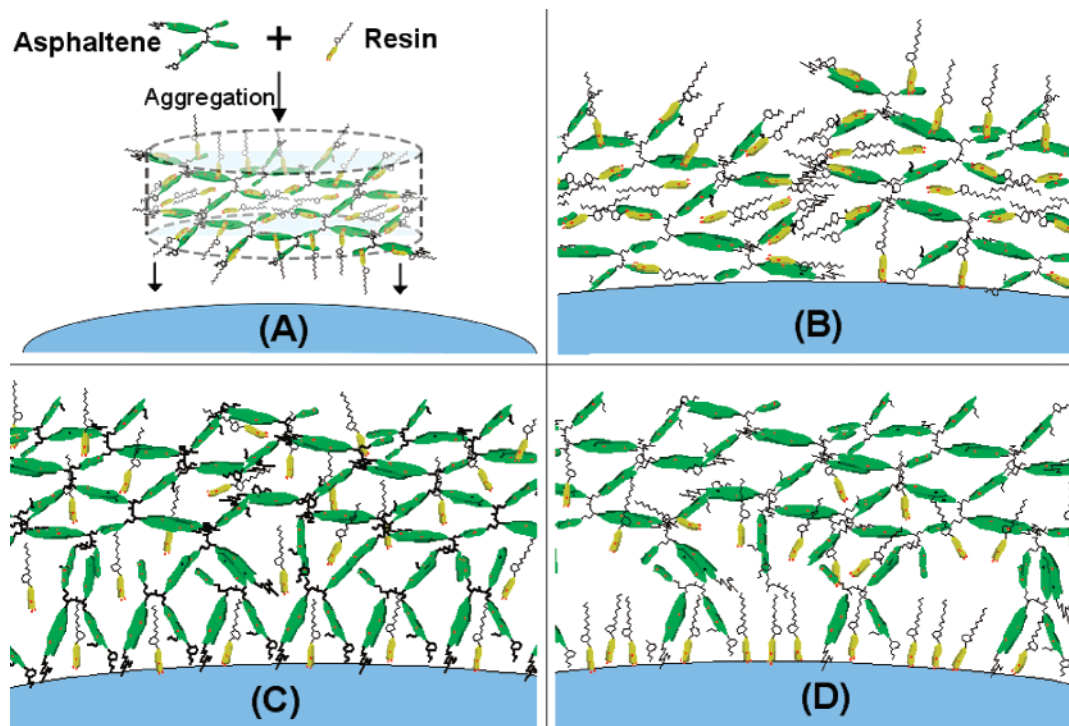


Figure 9. (A) Asphaltenes and resins co-aggregating into polydisperse oblate cylindrical aggregates and diffusing to the O/W interface. Whereupon, the aggregates (B) adsorb and begin to consolidate into a film. (C) Internal resins reptate through the film to the interface and (D) replace most asphaltene contacts at the interface.

Figure 9. This could lead to an elasticity maximum like the one we observe, as opposed to monotonic growth to values below that of the asphaltene-only system. This disruption of the asphaltene network results in the lower overall elasticity observed in Figures 7 and 8.

4. Conclusions

The results presented in this work identify the critical electric field technique as a useful tool to quantitatively gauge emulsion stability. We observed in the CEF experiments that the oil-phase asphaltene concentration significantly influenced the emulsion stability. For asphaltene-rich model oils, the emulsion system rapidly achieved the long-time stability within the first few hours. When both resins and asphaltenes were present, the resulting emulsion stability gauged by CEF was dependent on the R/A ratio and the interaction between asphaltenes and resins. These complex interactions between asphaltenes and resins result in a dynamic replaceable adsorption process for asphaltene and resin molecules at O/W interfaces. This may then allow for the formation of somewhat more stable emulsions in mixed asphaltene/resin systems at specific compositions and aging times.

Interfacial dilatational rheology experiments performed on O/W interfaces with asphaltene-only and asphaltene/resin mixtures exhibited similar qualitative trends compared to CEF. In these rheology experiments, however, asphaltene/resin mix-

tures *always* produced films with lower dilatational moduli than those of asphaltene-only solutions. The time dependent local maximum in the dilatational modulus for the mixed B asphaltene/B resin systems was dependent on the total adsorbate concentration despite a constant R/A of 0.5. These observed interfacial phenomena suggest that a dynamic adsorption/replacement process occurs during film formation for the mixed asphaltene/resin systems studied here. Reptation of resins adsorbed to aggregates through the asphaltenic network is a plausible limiting step, allowing for significant film consolidation before interfacial replacement and the observed maximum film elasticity.

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