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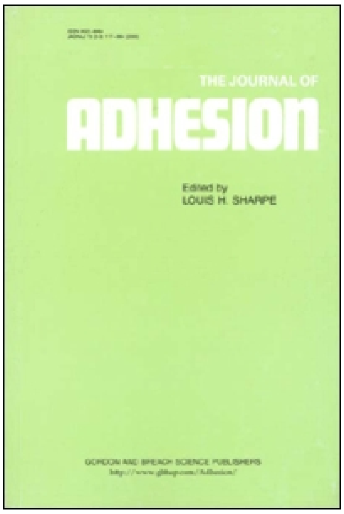

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RELAXATION OF ASPHALTENES AT THE TOLUENE/WATER INTERFACE: DIFFUSION EXCHANGE AND SURFACE REARRANGEMENT

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RELAXATION OF ASPHALTENES AT THE TOLUENE/WATER INTERFACE: DIFFUSION EXCHANGE AND SURFACE REARRANGEMENT

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Upon adsorption at the oil/water interface, asphaltenes slowly form a glassy interphase. This robust, asphaltene-rich interphase is likely the reason for prolonged stability of crude oil/water emulsions and for the propensity of asphaltenic crude oils to alter the wettability of reservoirs. Here we adopt interfacial dilatation rheology using the oscillating pendant drop with axisymmetric drop shape analysis (ADSA) to investigate the relaxation mechanisms of asphaltenes adsorbed at the toluene/water interface. We compare classical viscoelastic models with the measured rheologic data and find that the frequency response of the dilatational moduli fits a combination of diffusion-exchange and surface-rearrangement mechanisms. The combined relaxation model is verified by solvent washing the asphaltenes from the interface and measuring the dilatational response of the resulting irreversibly adsorbed species. After washout, the oil-phase diffusion component of the frequency response disappears, and the relaxation time of the adsorbed film increases by an order of magnitude. Since the studied asphaltenes prove insoluble in the synthetic aqueous brine (pH = 8.0), this result suggests that reversibly exchanging species in the oil phase weakens an interconnected asphaltene-gel/glass phase at the interface. Our experiments show, for the first time, that most of the surface-active asphaltenic molecules are irreversibly adsorbed from the oil phase.

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One of a collection of papers honoring A. W. Neumann, the recipient in February 2004 of *The Adhesion Society Award for Excellence in Adhesion Science, Sponsored by 3M*.

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INTRODUCTION

Since the early 1950s, researchers have recognized that asphaltenic crude oil–water interfaces form rigid skins [1–3]. Such interfacial films are postulated to result from irreversible adsorption and aggregation of asphaltene molecules via hydrogen and π–π aromatic ring bonding at the fluid–fluid interface [4, 5]. The prolonged stability of crude oil emulsions has been directly attributed to skin formation [4–8]. Likewise, we previously demonstrated that upon oil-drop adhesion to a brine-immersed mineral surface, advancing contact angles depend strongly on prior aging of the crude oil–water interface, consistent with the slow development of viscoelastic interfacial films [9]. Thus, investigation of interfacial-film viscoelasticty is crucial to understanding the development of mixed wettability in oil reservoirs.

As evident from dynamic interfacial-tension experiments [9–11], adsorption and rearrangement of surface-active macromolecular crude-oil components occur slowly (*i.e.*, on the order of days) at both the air–oil and oil–water interfaces. Nevertheless, most studies of asphaltenes at oil–water interfaces are restricted to interfacial aging times of less than 1 h [12–16]. For skin-forming systems, however, much longer times are needed to probe the progressive building and slow relaxation of adsorbed and aggregated multilayers [10, 11]. Subtle structural changes that occur in the interface over long time periods can be investigated using interfacial shear and dilatational rheology [9, 17, 18].

At both the air–crude oil [10] and crude oil–water [9, 15] interfaces, the dilatational moduli change more substantially upon interface aging than does the interfacial tension. This has also been found at the crude oil–water interface using shear rheology [19, 20]. Visual observation of interfacial skins upon compression of the asphaltenic crude oil–water interface correlates with large shear viscosities [19] and dilatational storage moduli [9, 21] that grow slowly in time.

The multitude of surface-active species in crude oils undoubtedly leads to mixed adsorption. Hence, relaxation of a dilated crude oil–brine interface occurs through multiple mechanisms with different characteristic times. Determination of the specific relaxation mechanisms requires the rheological response over a broad experimental time scale (*i.e.*, the frequency spectrum of the interfacial moduli) [22]. Following the pioneering work of Neumann and coworkers [23–26], we use axisymmetric drop shape analysis (ADSA) to measure the

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interfacial stress of a pendant-drop in dilatational deformation. Both small amplitude oscillatory flows and stress relaxation after a sudden strain displacement are imposed to probe broad experimental time scales (20 s to 2 h). This allows investigation of the contributions to the dilatational moduli from distinctly different surface-active species present in a model crude oil.

EXPERIMENTAL

Asphaltenes were extracted from a crude oil, designated as Crude AH with properties discussed elsewhere [9], according to ASTM method D2007-98 (*i.e.*, precipitated with n-heptane). Precipitated asphaltenes must be repeatedly dissolved into toluene and subsequently reprecipitated with n-heptane to remove resin molecules bound to asphaltene aggregates [27]. Here, we use a single precipitation step and wash the asphaltenes with n-heptane until the effluent is colorless. Therefore, some surface-active resins and smaller molecular weight asphaltenes are likely present in our extracted asphaltene sample. The model oil is prepared by dissolving extracted asphaltenes into toluene. Reagent-grade n-heptane (Burdick and Jackson, Muskegon, MI, USA) and toluene (Sigma, St. Louis, MO, USA) were used as received, and 1.0-M synthetic-sea-water (SSW) brine solutions (pH 8.0 ± 0.1) constituted the aqueous phase. Water was distilled and subsequently purified using a Milli-Q filtration unit (greater than 18.2 MΩ·cm resistivity). A liter of SSW contains 24.0047 g of NaCl, 1.4673 g of both $CaCl_2(2\ H_2O)$and $MgCl_2$ $(6\ H_2O)$, 3.9163 g of Na_2SO_4, and 0.0382 g of $NaHCO_3$ [28]. All salts used in the synthetic brine are from J. T. Baker Chemical (Phillipsburg, NY, USA) and are of analytic grade. They are used as received. The toluene/SSW interfacial tension remained constant at a value 36 mN/m for 24 h, confirming the absence of surface-active impurities. All experiments were conducted at 23°C.

To determine the dynamic interfacial tension of the model crude oil–water interface we use pendant-drop tensiometry with the more-dense water drop formed downwards at the tip of a stainless-steel needle (3.6 mm in diameter) immersed in the model crude oil. Using toluene as the continuous phase restricts asphaltene concentrations to below 0.01 wt% so that the pendant drop can be visualized optically. The homebuilt apparatus combines both the interfacial tension and interfacial dilatational rheology measurements and is discussed elsewhere [9, 29, 30]. Because we use toluene as the continuous phase, the cuvette is sealed with a stainless-steel lid to prevent compositional changes of the model oil through evaporation. The model crude oil is equilibrated with the brine for 24 h prior to performing experiments.

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After forming a fresh oil drop at the needle tip, the dynamic tension is followed in time using axisymmetric drop-shape analysis [23–26]. Image acquisition and regression of the interfacial tension is performed with commercially available Dropimage© software by fitting the Laplace equation to the drop shape. Typical precision in tension is ±1%.

We measure the surface dilatational storage modulus, E', and the surface dilatational loss modulus, E'', by subjecting the oil–water interface to infinitesimal periodic area deformation. Additionally, we measure the interfacial dilatational relaxation modulus, $E\ (t)$, after a step-strain deformation.

The oscillating-drop technique provides means to dilate an element of interfacial area [31]. We report the complex interfacial dilatational modulus, $E^*(\omega)$, which is defined as the linear proportionality factor between a periodically applied strain and the response stress

$$\Delta\bar{\gamma}e^{i(\omega t+\phi(\omega))} = E^*(\omega)\frac{\Delta A}{A_0}e^{i\omega t}, \tag{1}$$

where A_o is the unperturbed oil-drop interfacial area, ΔA is the amplitude of interfacial area change, ω is the oscillation frequency, ϕ is the phase-angle difference between the applied stress and response strain, and $\Delta\bar{\gamma}$ is the amplitude of the isotropic oil–water interfacial stress (measured from axisymmetric drop-shape analysis). The isotropic interfacial stress, $\bar{\gamma}$, is distinguished from the thermodynamic interfacial tension, γ, in that it generally includes nonequilibrium contributions (*i.e.*, diffusion and viscous dissipation) [32]. Since the drop area oscillates periodically, the dilatational modulus exhibits two contributions: an elastic part accounting for the recoverable energy stored in the interface (storage modulus, E') and the viscous part accounting for energy lost through relaxation processes (loss modulus, E''). The interfacial storage and loss moduli correspond to the real and imaginary components of the complex dilatational elasticity, $E^* = E' + iE''$.

Modification of a pendant-drop tensiometer enables sinusoidal variations in the drop surface area. Oscillation hardware consists of a 50 mL gas-tight syringe mechanically coupled to a linear piezoelectric actuator (Model P-840.3) from Physik Instrumente (Waldbronn, Germany). Actuator motion is forced using a function generator (Model 3325 A) from Hewlett-Packard (Palo Alto, CA, USA) that is computer controlled with National Instruments (Austin, TX, USA) LabView software. The piezoelectric actuator is capable of subnanometer resolution, ensuring the smoothest possible drop-volume oscillation.

Interfacial moduli are measured after 24 h of aging. The frequency dependencies of the dilatational moduli are determined by varying the oscillation frequency from 0.01 to 3.14 rad/s. Equation (1) and Equation (2) demand small strains so that the interface lies in the linear viscoelastic regime. We set $\Delta A/A_o$ at 2.5%, since nonlinear effects are observed above a relative strain of about 5.0%. In order to maintain a Laplacian shape for the oscillating drop, we restrict the oscillation frequency to below 1.57 rad/s [30, 33].

To determine the dilatational relaxation modulus, $E\,(t)$, we measure the stress relaxation after a sudden strain displacement. In these experiments, the interface is instantaneously deformed (*i.e.*, compressed) and then held constant in area while the interfacial tension is measured. The dilatational modulus is calculated as a function of time from the following expression

$$E(t) = \Delta\bar{\gamma}(t)\frac{A_o}{\Delta A}, \tag{2}$$

where $\Delta\bar{\gamma}$ is the difference between the measured isotropic interfacial stress and the tension prior to interfacial deformation. The dilatational relaxation modulus, $E\,(t)$, is related to the complex dilatational modulus, $E^{*}(\omega)$, by

$$E'(\omega) = E_\infty + \omega\int_t^\infty (E(t) - E_\infty)\sin(\omega t)dt \tag{3}$$

and

$$E''(\omega) = \omega\int_t^\infty (E(t) - E_\infty)\cos(\omega t)dt, \tag{4}$$

where $E_\infty = d\gamma/d\ln A$ is the static modulus (zero frequency response) [34] or the static Gibbs elasticity of the irreversibly adsorbed species. The Fourier transforms are performed by numerically integrating the experimental data. Error generated as a result of the numerical integration and, hence, error in the transformed moduli increases nonlinearly with frequency and is a function of the relaxation time (error is negligible for frequencies less than 0.005 rad/s in this work). The advantage of the step-strain technique is that the low frequency response can be determined directly from the relatively quick decaying relaxation modulus (the interfacial stress response decays to a steady value within 2 h for the systems investigated in this work). To acquire the same breadth in the relaxation spectra using the oscillatory technique requires a very long period of time because of the low frequencies needed to probe slow stress relaxation. As with the complex

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modulus, we set $\Delta A/A_o$ at 2.5% to remain in the linear viscoelastic regime.

RESULTS AND DISCUSSION

Figure 1 reports the dynamic interfacial tension, $\gamma(t)$, on a semilogarithmic scale for the model crude oil immersed in SSW. The observed trend is qualitatively similar to that reported for the original crude oil (Crude AH) from which the asphaltenes were extracted [9]. Initially, the tension decays from 36 mN/m (toluene–SSW interfacial tension) to approximately 27 mN/m after 0.5 h of interface aging at which point there is a subtle slope change, suggesting a transition to interfacial-network formation [35]. The long time scales for tension lowering in Figure 1 are reminiscent of those of large molecular weight species that require long relaxation times for adsorption and reconfiguration at interfaces [35, 36]. When oil-equilibrated brine was replaced by fresh brine not contacted by the crude oil from which the AH

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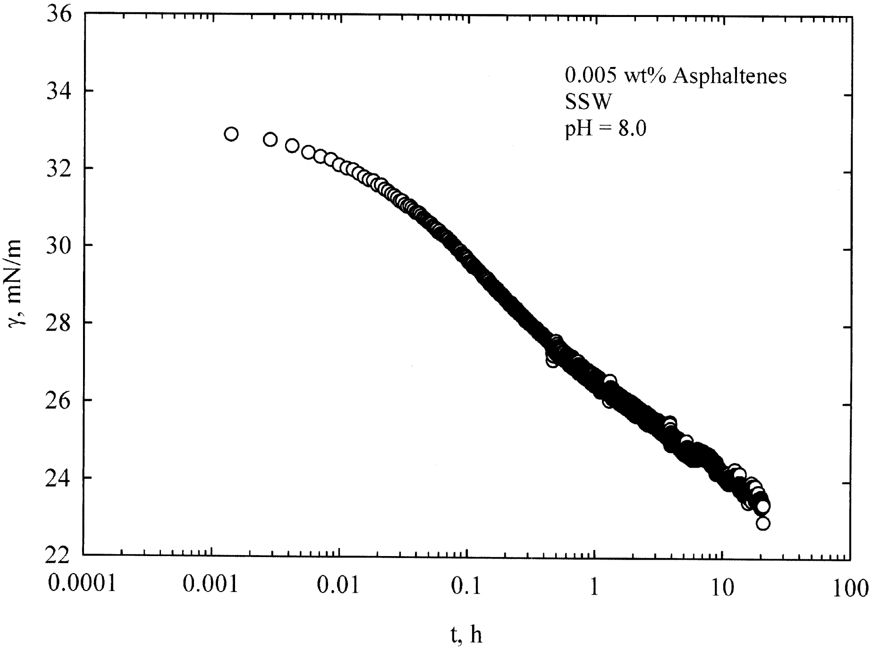

FIGURE 1 Dynamic interfacial tension of the model crude oil–water interface.

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asphaltenes were extracted, no rise in tension is observed [9]. Hence, none of the asphaltenes desorb into the aqueous phase at the brine composition and pH employed here. Apparently, oil-soluble asphaltenes produce surface network structures that slowly evolve at the oil/water interface. If the oil droplet in Figure 1 is retracted after 24 h of aging, a rigid, wrinkled skin is clearly visible. However, the wrinkles are relatively short lived, and after the initial retraction the drop slowly relaxes back to a shape similar to that prior to retraction in approximately 10 min.

Figure 2 shows, as closed circles, the dilatational relaxation modulus, $E\,(t)$, for asphaltenes adsorbed at the toluene/water interface after aging for 24 h (after-washout data in Figure 2 are discussed later). Immediately upon compression, the stress in the interface is high. As the adsorbed asphaltene molecules rearrange, the dilatational relaxation modulus decays in time. In Figure 2, the modulus decays to a nonzero value denoted by E_∞, where the subscript, ∞, indicates

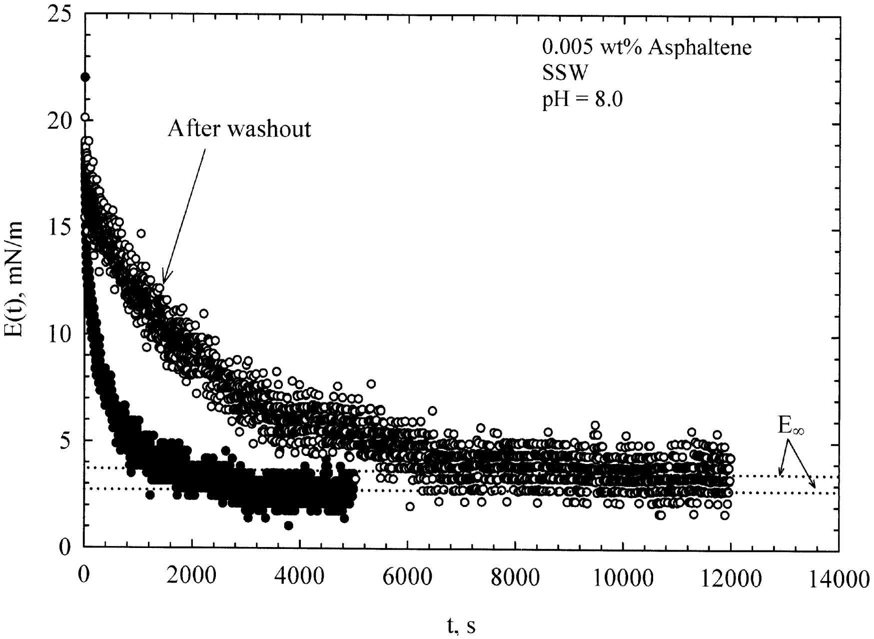

FIGURE 2 Dilatational response after a 2.5% step compression of the model crude oil–water interfacial area. The interface was aged for 24 h before the compression (closed circles). After washout, the open circles show the dilatational response of the irreversibly adsorbed species.

zero-frequency (*i.e.*, $t \to \infty$). This means that the interfacial tension after compression is not the same as the initial value. A caveat of the stress-relaxation technique, as applied to our dynamic experiments, is that the structure of the interface layer must not age appreciably during the course of the relaxation experiment. We assert that this condition is fulfilled when the interfacial stress change due to compression is much faster than the interfacial tension change due to aging (*i.e.*, the slow surface pressure changes seen in Figure 1).

Figure 3 shows the interfacial dilatational storage and loss moduli as a function of frequency on a semilogarithmic scale after aging the oil–water interface for 24 h. The dilatational storage and loss moduli measured using the oscillatory technique are shown as closed and open triangles, respectively. Dilatational storage and loss moduli calculated from $E\ (t)$ using Equations (3) and (4) are shown as closed and open circles, respectively. Excellent matching of the dilatational

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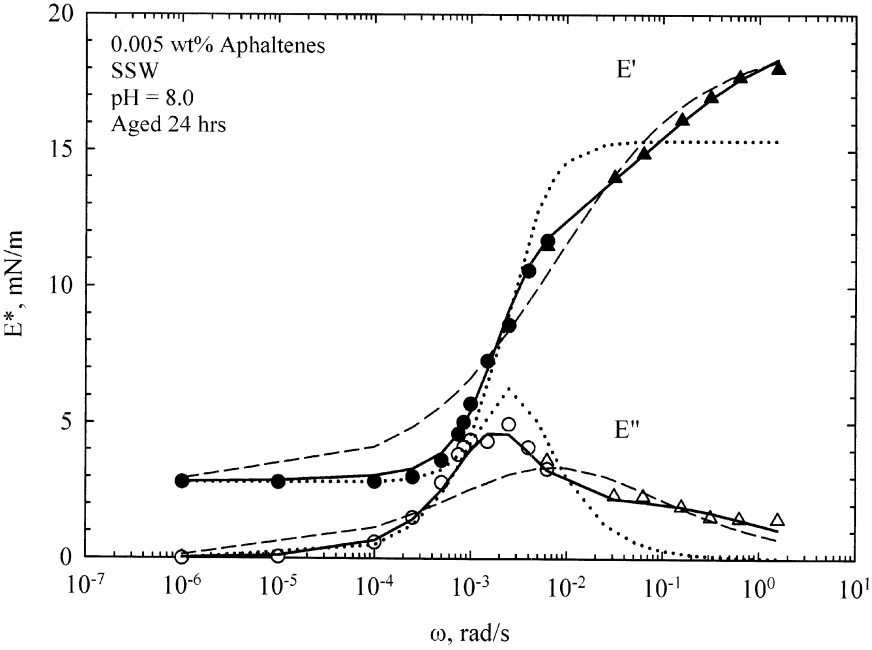

FIGURE 3 Interfacial dilatational moduli after 24 h of aging the model crude oil–water interface. The storage and loss moduli are shown as closed and open symbols. Triangles represent data collected using the oscillatory technique and circles represent transformed step-strain data. The dashed line is the modified LVDT model, the dotted line is the Maxwell model, and the solid line is the composite model.

moduli using the two different techniques is established at 0.00628 rad/s. Combination of the two techniques thus exposes relaxation processes that occur over six frequency decades. In the zero-frequency limit, the dilatational storage modulus is finite and corresponds to E_∞ in Figure 2. A static storage modulus is characteristic of irreversibly adsorbed surface-active species [37, 38]. As the frequency increases, the dilatational storage modulus increases sharply and then begins to level off at higher frequencies. The loss modulus initially increases until $\omega = 2.5 \times 10^{-3}$ rad/s, reaches a maximum, and then decreases. The frequency responses of E' and E'' are characteristic of relaxation processes that include multilayer exchange kinetics [22], diffusion exchange [39], and surface relaxations (*i.e.*, Maxwell response [37, 38, 40–42]). We model the experimental data in Figure 3 to discern the specific relaxation mechanisms of the adsorbed asphaltenes.

Because of the complexity of surface-active species present in heavy crude oils [12], it is likely that the adsorbed molecules relax through several different mechanisms. Assuming that physical exchange can occur for small resin and asphaltene species between the interface and bulk model crude oil, the frequency response of the dilatational moduli are given by a modified form of the Lucassen and van den Temple model (LVDT) [39] for diffusion exchange of reversibly adsorbed surfactant-like molecules:

$$E' = E_\infty + E_o \frac{1+\Omega}{1+2\Omega+2\Omega^2}, \tag{7}$$

where

$$E'' = E_o \frac{\Omega}{1+2\Omega+2\Omega^2}, \tag{8}$$

where $\Omega = (\tau_D \omega)^{-1/2}$ is a dimensionless parameter consisting of the ratio of the experimental and diffusion time scales, τ_D is the characteristic time for diffusion, $E_o = -d\gamma/d\ln\Gamma$ is the Gibbs elasticity for reversibly adsorbed species, and Γ is the interfacial concentration of the reversible surface-active species. Our embodiment of the LVDT model in Equations (7) and (8) includes the static Gibbs elasticity of irreversibly adsorbed asphaltenes, E_∞. To accentuate the role of reversibly adsorbed surfactant-like molecules, surface relaxation of the irreversibly adsorbed species is not included. Thus, E_∞ is simply a shift factor for the storage modulus directly determined from the experimental data (see E_∞ in Figure 2). The parameters τ_D and E_o were regressed to the experimental data. The resulting modified LVDT

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model from Equations (7) and (8) is shown as dashed lines in Figure 3. This model fits E' and E'' at frequencies greater than 0.0314 rad/s but fails to predict the entire measured frequency response. Consistent with the experimental data at high frequencies, the modified LVDT model successfully fits the broad-stretched frequency response. Accordingly, the LVDT analysis confirms that some smaller reversibly adsorbed resins/asphaltenes exchange with the bulk model crude oil. However, quantitative disagreement with the measured frequency response of E' and E'' suggests additional relaxation processes at low frequencies.

Visual observation of interfacial skins strongly suggests that slow surface relaxation of the irreversibly adsorbed asphaltenes contributes to the dilatational response. For insoluble monolayers, the frequency response of the dilatational moduli has been shown to agree with a Maxwell model [37, 38, 41]. Hence, we write for the irreversibly adsorbed asphaltenic film that

$$E' = E_\infty + E_M \frac{\tau_M^2 \omega^2}{1 + \tau_M^2 \omega^2} \tag{9}$$

and

$$E'' = E_M \frac{\tau_M \omega}{1 + \tau_M^2 \omega^2}, \tag{10}$$

where τ_{M} is the characteristic surface relaxation time and E_M is the high-frequency limiting modulus (*i.e.*, $\omega \to \infty$). Again E_∞ must be included to account for the static or Gibbs elasticity of the irreversibly adsorbed species. Upon best fitting the parameters τ_{M} and E_M, Equations (9) and (10) are plotted in Figure 3 as dotted lines. This model fits the data well at frequencies below 2.5×10^{-3} rad/s. The major difference between the two rheologic models is that the change in moduli occurs in a narrower frequency range for the Maxwell model compared with the modified LDVT model. Neither model predicts the entire experimentally measured frequency response of the dilatational moduli, but each fits the data well within a finite frequency range. If the two classes of relaxation processes are independent, then the response can be modeled as a linear combination of the individual responses [43]. A simple additive model is plotted in Figure 3 as a solid line. Although this model requires regression of four parameters, E_o, E_M, τ_D, and τ_{M} (E_∞ is determined from Figure 2), it is able to fit both dilatational moduli with very little residual error. Regressed parameters are shown in Row 1 of Table 1. The high-frequency limiting moduli (E_o and E_M) are comparable, but the relaxation time for the Maxwell

TABLE 1 Regressed Interfacial Rheology Model Parameters

System	E_∞ (mM/m)	E_o (mM/m)	τ_D(s)	E_M (mM/m)	τ_M (s)
Prewashout	2.8	9.0	25	7.9	570
Postwashout	3.9	—	—	13.3	2223

relaxation mode is an order of magnitude greater than that of the corresponding LVDT mode.

To ascertain whether sorption kinetics contributes to the second, low-frequency relaxation mode in Figure 3, we utilize continuous flow tensiometry (CFT) [44]. Ten cell volumes of asphaltene-free toluene (interfacial tension 36 mN/m) were flushed through the optical cuvette of the tensiometer, resulting in a negligible bulk asphaltene concentration in the toluene solvent. Following washout, stirring was stopped, and the tension was monitored for an additional 18 h. The result of this experiment is shown in Figure 4. Three time regimes, separated by vertical dashed lines, are labeled in the figure. These

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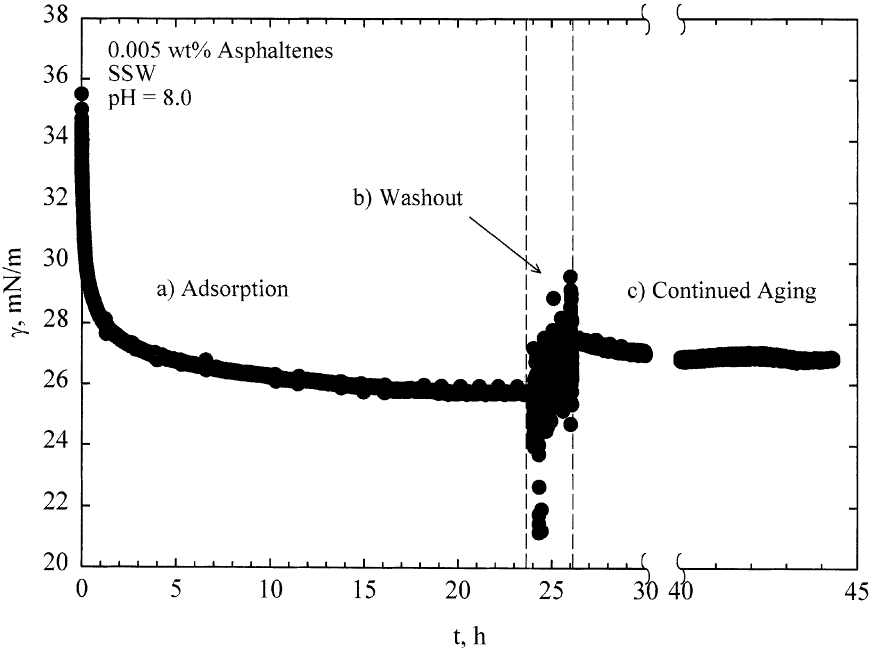

FIGURE 4 Washout of asphaltenes at the toluene–water interface. SSW, pH = 8.0.

regimes include: a) adsorption, b) washout, and c) continued aging after complete depletion of asphaltene from the bulk toluene solution. The washout experiment was started after 24 h of interface aging. Scatter in the interfacial tension observed during washout is an artifact of drop vibration due to stirring of the continuous toluene phase [44]. There is a break along the abscissa shown to emphasize the period of pure solvent contact (almost 20 h). Washing away the reversible surface-active asphaltene species increased the tension by only 1.5 mN/m. In addition, no appreciable change in the interfacial tension was observed 18 h after the washout. Upon compression of the washed drop, a long-lasting interfacial skin was visually observed giving the first evidence that rigid skins seen in crude oil systems [2, 3] result primarily from irreversible asphaltene adsorption. Also, the discrepancy between the LVDT model and the low-frequency data reported in Figure 3 is not due to sorption kinetics but rather surface relaxation of irreversibly adsorbed and aggregated asphaltenes.

Directly after washout, both linear oscillatory and step-strain rheology experiments were performed. The resulting interfacial dilatational storage and loss moduli are plotted in Figure 5 as a function of frequency on a semilogarithmic scale. As before, the dilatational storage and loss moduli measured using the oscillatory technique are shown as closed and open triangles, whereas dilatational storage and loss moduli calculated from $E(t)$ in Figure 2 (using Equations (3) and (4)) are shown as closed and open circles, respectively. The surface rheological response is substantially different from that observed before washout in Figure 3. First, the majority of the change in the storage modulus occurs within one frequency decade *versus* 3 frequency decades prior to toluene washout. In addition, the loss modulus shows a single sharp peak and the broad relaxation at higher frequencies mostly disappears, suggesting that the response is dominated by a single relaxation mode in the frequency range probed. The data are fit to the Maxwell model with regressed parameters shown in Row 2 of Table 1. There is no need to include a LVDT relaxation mechanism. It is clear that some fraction of the adsorbed asphaltene molecules desorbed from the interface during washout, as evidenced from both the rise in tension in Figure 4 and the response of the moduli in Figure 5. The surface rheological transition after washout is striking. The interface becomes much more solid-like and the characteristic relaxation time, τ_M, is now an order of magnitude larger than that observed prior to washout. Apparently, the smaller asphaltene or resin molecules that can be solvent washed from the interface act as solubilizers to soften the irreversibly adsorbed viscoelastic interfacial network.

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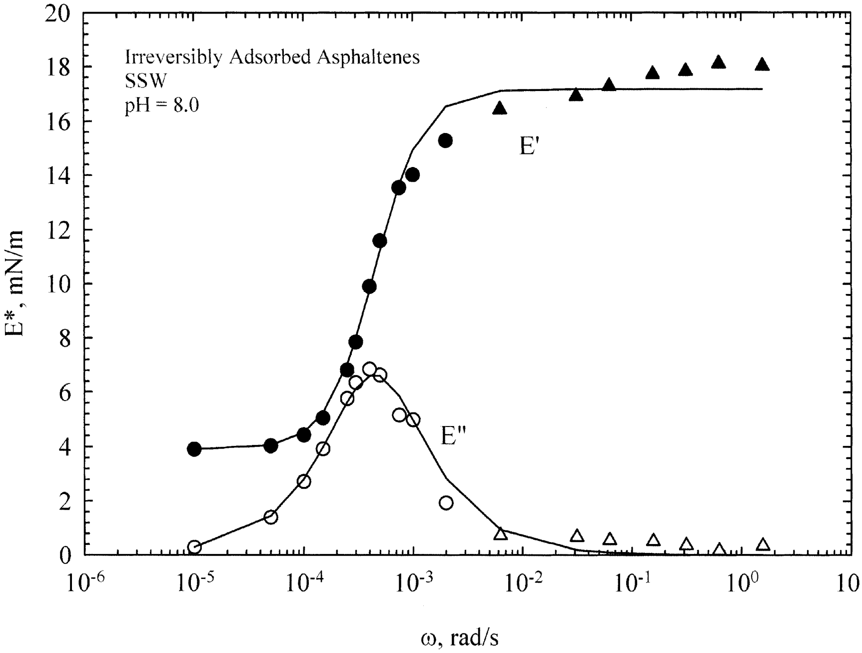

FIGURE 5 Interfacial dilatational moduli of the irreversibly adsorbed asphaltene fraction after 24 h of aging the model crude oil–water interface. The storage and loss moduli are shown as closed and open symbols, respectively. Triangles represent data collected using the oscillatory technique and circles represent transformed step-strain data from Figure 2 (open circles). The solid line corresponds to the Maxwell model.

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Comparison of Figures 3 (before washout) and 5 (following washout) reveals several points. The low frequency data demonstrate that the irreversibly adsorbed and aggregated asphaltenic film is much more rigid based on the order of magnitude larger relaxation time, τ_M, than that observed before washout. However, the magnitudes of the dilatational storage and loss moduli at a single frequency, 0.1 rad/s (c.f. Figures 3 and 5), suggest that the interfaces are rheologically similar (the magnitudes of the moduli are nearly identical). Therefore, when comparing different crude oils, caution must be taken before drawing conclusions about the structure of the adsorbed layer based only on magnitudes of measured moduli at a single frequency.

For crude oils, model and actual, the oil–water interfacial viscoelastic properties change strongly with oil composition, asphaltene and resin content, and interface aging [9, 15, 19, 20, 29, 45]. Therefore,

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the particular interfacial viscoelastic parameters reported in Table 1 apply only to Crude AH asphaltenes solubilized in toluene and in dilute amounts. The contribution to the elasticity of the asphaltenic skin (*i.e.*, as gauged by the magnitudes of E_M and E_o) and the magnitudes of the irreversible and reversible relaxation times (*i.e.*, τ_M and τ_D) are expected to be highly system and age specific. Nevertheless, we argue that the basic picture of mixed-mode dilatational relaxation (*i.e.*, reversible and irreversible) remains valid. Since toluene is a good solvent for asphaltenes, it was somewhat surprising that the present AH asphaltenes dissolved in toluene do indeed demonstrate both interfacial skins, albeit weaker than those from actual crude oils [30], and irreversible adsorption at the oil–water interface. Based on these two findings and on the long tension aging times seen for crude oil–water water interfaces [9, 30], we suggest that the irreversible fraction of asphaltenes adsorbed at the crude oil–water interface is both more pronounced and more robust than that reported here for the model toluene oil. Although actual crude oils have higher asphaltene concentration and lower asphaltene solubility than our model oil, some reversible diffusion exchange with the bulk oil can still be present. Indeed, we observed diffusion exchange in linear oscillatory dilatational deformation of the oil–water interface with the crude oil from which the present Crude AH asphaltenes were extracted [30]. Presumably, the lower molecular weight asphaltenes and the resin component reversibly exchange with the crude oil. Accordingly, actual crude oil–water interfaces can also be expected to follow mixed-mode relaxation mechanisms with increased resin content softening the interface and enhancing reversible exchange.

CONCLUSIONS

We employed a model oil system consisting of asphaltenes precipitated from a heavy crude oil and dissolved in toluene. The dynamic interfacial tension was similar to that observed for the original crude oil from which the asphaltenes were extracted [9]. After aging the interface for 24 h, an interfacial skin was observed visually upon compression of the model crude oil/water interface.

The interfacial film was investigated noninvasively using interfacial dilatational rheology. By combining the oscillating and step-strain pendant-drop techniques, relaxation mechanisms were investigated over a range from 1×10^{-5}–1.57 rad/s. We found that the linear viscoelastic response fits a combination of a modified LDVT diffusion-exchange model and a Maxwell surface-relaxation model. The combined model was verified by exchanging the toluene model crude oil with fresh asphaltene-free toluene. Upon washout, the interfacial tension increased only by 1.5 mN/m, indicating that the majority of asphaltenes are irreversibly adsorbed and that only a small fraction desorbs into the fresh toluene. The relaxation time of the interface after washout increased by an order of magnitude, suggesting that the reversibly adsorbed species disrupt asphaltene aggregation at the interface, resulting in a more tenuous and weaker network structure. These experiments show, for the first time, that most of the asphaltene molecules are irreversibly adsorbed with respect to both the oil and water phases.

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