Interfacial Viscoelasticity in Crude Oil-Water Systems To Understand Incremental Oil Recovery

Ahmed M. Saad, King Abdullah University of Science and Technology, Stefano Aime, Harvard University, Sharath C. Mahavadi, Schlumberger-Doll Research, Yi-Qiao Song, Schlumberger-Doll Research and Massachusetts General Hospital, Tadeusz W. Patzek, King Abdullah University of Science and Technology and David Weitz, Harvard University

Abstract

Improved oil recovery from asphaltenic oil reservoirs may provide the world with a significant source of lower-cost energy over many decades. However, the mechanisms through which the surface-active components in crude oil, such as asphaltenes and organic acids, affect incremental oil production are still unclear.

In this study, we investigate crude oil/water interfacial films using shear and dilational rheology for mechanical properties and Fourier-Transform Infrared Spectroscopy (FTIR) to better understand its molecular species present at the interface that contribute to the development of viscoelastic behaviors. Dilational rheology has proven to be more sensitive to early time development of elasticity. In contrast, shear rheology provided more insights regarding the formation of elastic films at the macroscopic scale and late time interfacial changes. The presence of salts such as sodium chloride in the aqueous phase played a critical role in altering the dynamics of both the rheological properties development and the interfacial tension.

Introduction

Crude oil consists of a wide range of components with different chemical characteristics. Researchers have discovered that crude oils rich in asphaltenes form interfacial elastic films when in contact with water (Strassner et al., 1968; Reisberg and Doscher, 1956; Freer and Radke, 2004). Following primary drainage in oil reservoirs, these interfacial films play an important role in altering the wettability of the reservoir pores as some of them break, stamping parts of the rock surface, and making it more oil-wet. This leads to the development of what is known as mixed-wettability, where portions of the pores are water-wet, mainly in sharp corners and within roughness, and other portions oil-wet (Kovscek et al., 1993). Such a wettability state makes it more challenging to produce the oil, affecting primary and secondary oil recovery (Yan et al., 1997; Kaminsky and Radke, 1998). Besides, the interfacial films have been shown to affect emulsion stability, which is a major concern for flow assurance, processing, and quality of final products (Sjöblom et al., 2003; Lesaint et al., 2009).

Studies have shown that salinity correlates with the shear elasticity modulus (Moradi and Alvarado, 2016). The impact of the viscoelastic films on fluid dynamics has been studied in 2D micro-models, investigating pore-scale events, such as snap-off. It was observed that the interfacial films formed against lower salinity brines, lead to larger droplet size after snap-off (Alvarado et al., 2014). Nevertheless, the mechanisms through which different ionic species and the salinity of the aqueous phase contribute to the evolution of the interfacial viscoelasticity and
the chemical composition of the interfacial films that is responsible for this behavior is not very clear. A better understanding of these mechanisms at both macroscopic and molecular levels is invaluable to design and fine-tune better enhanced oil recovery strategies of achieving higher incremental oil recovery.

In our study, we combine dilational and shear rheology techniques to gain insight into the molecular processes occurring at the interface. The interfacial film material is analyzed using FTIR to probe for its chemical constituents. We vary the chemical composition of the aqueous phase from de-ionized water (DI) water to sodium chloride solutions to investigate how ions in the aqueous phase interact with the surface-active species in the crude oil.

Materials and Methods

Chemicals. Deionized water was obtained from a Milli-Q water system (Synergy, EMD Millipore Corporation), giving resistivity greater than 18.2 MΩ.cm at 25°. Toluene (99.9%, Fisher Chemicals) was used as received to dilute the crude oil. In all of our studies, we used 3 wt% crude oil in toluene, freshly prepared prior to each experiment. The two fluids were mixed using a vortex mixer for 1 min. The SARA composition of the crude oil was obtained using IP-143 method, and is presented in Table 1 along with other physical and chemical properties.

<table>
<thead>
<tr>
<th>Saturates</th>
<th>38.3 wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatics</td>
<td>19.8 wt%</td>
</tr>
<tr>
<td>Resins</td>
<td>36.6 wt%</td>
</tr>
<tr>
<td>Asphaltenes</td>
<td>3.97 wt%</td>
</tr>
<tr>
<td>Total Acid Number (TAN)</td>
<td>1.19 mg KOH/g</td>
</tr>
<tr>
<td>Density</td>
<td>0.955 g/cm³ @ 25°C</td>
</tr>
<tr>
<td>Viscosity</td>
<td>1290 cP</td>
</tr>
</tbody>
</table>

Table 1: SARA analysis and the physical properties of the crude oil.

Dilational rheology. Complex interfaces cannot be described solely by the interfacial tension, as there are additional energy costs of bending, shearing or stretching. When the interface expands, the dilational stress of an interfacial film can be defined as the change of the interfacial tension (γ) per unit relative change in the surface area (A). Surface elasticity, E, of the interface was defined by (Gibbs, 1931) as

\[
E = \frac{d\gamma}{d\ln A}
\]

(1)

For purely elastic interfaces, the interfacial tension response follows the area change instantaneously. In contrast, for complex viscoelastic interfaces, there can be some time delay between stress and strain. In this more general case, the modulus can be expressed as a complex value,

\[
E^* = E' + i \cdot E''
\]

(2)

where \(E'\) is the storage modulus, quantifying the elastic response of the film, whereas \(E''\) is the loss modulus that is proportional to the viscous dissipation.

The dilational rheology experiments provide information about the interfacial tension and the extensional viscoelasticity of the interface by monitoring the shape of an oil droplet in water as its volume is periodically perturbed with a prescribed amplitude and frequency. In our experiments, we use an optical tensiometer (Biolin Theta Flex TF300 with PD200 oscillating drop module), where the droplet volume is maintained using an automated syringe pump and fine-tuned by a piezo pump. The surface area, \(A(t)\), and the dynamic interfacial tension, \(\gamma(t)\) are calculated by processing the images of the oscillating drop and fitting the Young-Laplace equation to the shape of the interface (Ravera et al., 2010). An amplitude of 0.5% and a frequency of 0.1 Hz were used for all the dilational rheology experiments.
Shear rheology. Another type of interfacial measurements is the interfacial shear rheology, where a shear deformation is applied at a constant interfacial area, and the stress response is measured (Krägel and Derkatch, 2010). We used a Discovery Hybrid Rheometer (DHR) from TA instruments, equipped with the Double Wall Ring (DWR) interfacial geometry. A modified double wall ring cell was built to reduce the evaporation of volatile components in our fluids (Figure 1). The cell body was made of Teflon and the cap was made of aluminum and glass. All materials are chemically compatible with toluene and crude oil, to prevent any damage or contamination to the cell. The cap has a circular glass top with a hole at the center, which prevents evaporation, allowing visual inspection. There are two inlets and two outlets positioned at different elevations to allow circulation of the oil/toluene and water phases without disturbing the interface at the end of the experiment to collect the interfacial material as shown in Figure 1.

![Figure 1: Schematic of the custom-built interfacial shear rheology setup. The top inlet and outlet have metallic 90° bent needles of gauge 27. The lower two inlets have 1/16 inch PTFE tubes surrounded and wrapped with Teflon tape to prevent leakage.](image)

FTIR Spectroscopy. To study the chemical composition of the interfacial film, we performed FTIR spectroscopy measurements on the films collected at the oil-water interface. At the end of the shear rheology experiment, we injected pure toluene into the oil phase through the inlet at a low flow rate about 100 $\mu$L/min to flush the crude oil without damaging the film. Afterwards, we collected the interfacial film and transferred it to a glass vial. The excess solvent from the vial was removed slowly under nitrogen environment at low temperatures. FTIR spectra were recorded in the attenuated total reflectance (ATR) mode on a PIKE Technologies MIRacle ATR accessory bench and a Varian 670-IR FTIR spectrometer. Samples were deposited on the ATR crystal from a methylene chloride solution, and the solvent was allowed to evaporate. All the measurements were performed under a nitrogen blanket. Between the measurements, a blank was tested to ensure there was no contamination from the previous measurements.

Results and discussion

As discussed in the experimental section, the dilational rheology measurement is conducted by inflating a droplet of oil surrounded by the aqueous phase. To establish a base case, we compare the behavior of toluene/water to crude oil/water systems. After aging for 24 hrs, we completely retract the fluid droplet inside the syringe needle. As we do so, the toluene droplet shrinks gradually, maintaining a regular droplet shape at all times (Figure 2 [A]), whereas the crude oil droplet shape becomes irregular, developing wrinkles and buckling inside the needle, as shown in Figure 2 [B], thus demonstrating that an elastic skin had formed at the oil-water interface.
Dilational rheology. To gain a more quantitative insight into the origin and the properties of an elastic skin, we performed dilational rheology measurements on both systems to compare the elasticity modulus and the interfacial tension response. Both experiments are conducted with DI water as the surrounding phase. As expected, no elastic modulus could be measured on the toluene droplet, confirming that toluene does not develop any interfacial elasticity. By contrast, with dilute crude oil we observe that the surface elastic modulus grows quickly and reaches a plateau value about 10 hrs after the drop is formed (Figure 3 [A]). In addition, the crude oil exhibits a corresponding drop in interfacial tension, while toluene does not show any significant change of the interfacial tension over the full duration of the experiment (Figure 3 [B]). This observation strongly suggest that surface-active species in the crude oil slowly adsorb at the interface over the first few hours following the droplet formation, thereby leading to the development of elasticity and reduction of the interfacial tension.

Figure 3: [A] The dilational elasticity moduli for crude oil/DI water, toluene/DI water, and crude oil/0.1 M NaCl solution. [B] The corresponding dynamic interfacial tension response. Toluene does not develop elasticity or any significant change in interfacial tension.
Figure 4: [A] Oscillation strain sweep of the interfacial film formed against DI water at a frequency of 1 Hz. [B] The corresponding frequency sweep of the film at 0.1 % strain. We use 0.1 % strain and 1 Hz frequency for all the shear rheology experiments to ensure that the deformations are in the linear region and no damage occurs to the interfacial films.

Shear rheology. To investigate how the interfacial films behave under shear deformation at the constant surface area, we have performed shear rheology measurement. One of the advantages of such measurement is the larger scale of the investigated area, of the order of centimeters, probed by the ring in our setup, as explained in the experimental section. We perform a sweep of the oscillation strain and frequency for the interfacial film formed against DI water to optimize the parameters used in our shear experiments. The elastic modulus only shows a weak dependence on frequency, and the linear viscoelastic regime, where \( G' \) is independent of the amplitude, extends beyond 2% (Figure 4). We chose a very conservative 0.1 % strain and 1 Hz frequency for all of our shear rheology experiments to ensure that the oscillations stay within the linear elastic regime and prevent damage to the interfacial film. Similarly to the dilational modulus, the shear modulus of crude oil-water interface shows a monotonic build-up over time, confirming the formation of an elastic film at the interface. However, the onset of \( G' \) is delayed by about 10 hrs (Figure 5), significantly later than the observed rise in \( E' \) in the dilational rheology data (Figure 3). This time delay suggests that the formation of a system-spanning elastic network does not occur simultaneously with the adsorption process. It starts taking place after a significant delay. Indeed, shear rheology is essentially blind to molecule adsorption preceding the formation of an elastic film spanning the full, millimeter-scale gap between the ring and the walls. Our results suggest that two distinct dynamic regimes contribute to the onset of interfacial elasticity in crude oil-water systems. First, surface-active molecules adsorb at the interface, lowering the surface tension and contributing to the dilational modulus but not to the shear modulus. This process reaches a steady-state in about 10 hrs, as indicated by dilational rheology. On a significantly longer timescale, these molecules rearrange at the interface, forming a system-spanning network with a finite shear modulus \( G' \) that keeps increasing even after several days, suggesting slow aging dynamics typical of kinetically arrested materials, to which dilational rheology is essentially insensitive.

FTIR analysis. To gain insight into the molecular species involved in these processes, we collected and analyzed the interfacial material at the end of the shear rheology experiments. FTIR spectra of the crude oil and the collected interfacial material obtained are compared in Figure 6 [A]. The major difference between the crude oil and interfacial material is observed below 1800 cm\(^{-1}\). The most obvious difference is the presence of a peak for C=O vibration at 1702 cm\(^{-1}\), indicating the presence of carboxylic acid moieties in the interfacial compounds, that are essentially invisible in the bulk crude oil spectra. Figure 6 [B] highlights the methylene and methyl regions between 2500–3600 cm\(^{-1}\). This region indicates the absence of amine (-NH\(_2\)) groups in the interfacial films and
the presence of a broad peak at 3200 cm\(^{-1}\), representing the O-H group in carboxylic acids. This observation is consistent with similar observations in the literature Andersen et al. (2017).

However, the O–H peak in the crude oil is broader than the interfacial film peak in the same region, indicating the presence of other types of O-H and potential amine in the crude oil. This zoomed region also suggests the presence of aromatic C – H stretch (3050 cm\(^{-1}\)) and -CH\(_3\) groups on an aromatic ring (2727 cm\(^{-1}\)). Figure 6 [C] is a zoomed region between 1500–1900 cm\(^{-1}\) highlighting the presence of carboxylic acid group bearing molecules. The interfacial film shows a clear carboxylic acid peak at 1702 cm\(^{-1}\). When we consider the remaining part of the spectrum, it is obvious that the aromatic C=C stretch at 1600 cm\(^{-1}\) is much more prominent in the interfacial film compared to the original crude oil. The peak positions of C=O and C=C indicates that they are part of a conjugated system. However, when we examined the aliphatic region around 3000 cm\(^{-1}\), it is not clear whether the interfacial material has relatively more aromatic components in it or not.

To understand better the type of aromatic groups, we examined the fingerprint region between 650-1200 cm\(^{-1}\). In Figure 6[D] the regions between 650-900 cm\(^{-1}\) represent the degree of condensation of aromatic rings and also their substitution in fossil aromatic compounds. In the spectra, it is clear that except the 3H substitution, all the other aromatic rings are present in both crude oil and interfacial film. However, a close examination of the spectra reveals that around 750 cm\(^{-1}\), crude oil aromatics are more condensed than the interfacial film. The interfacial film indicates the presence of long aliphatic chains with a clear peak at 727 cm\(^{-1}\) and monosubstituted aromatic groups with a peak around 700 cm\(^{-1}\). If we consider peaks at 2727 cm\(^{-1}\) in conjunction with peaks at 700 and 727 cm\(^{-1}\), it is clear that interfacial films contain significant aromatic rings with single substitution. The difference between crude oil and interfacial film in the region between 750–650 cm\(^{-1}\) is clearly visible in the 2nd derivative of the spectra presented as an inset in Figure 6 [D]. In addition, the peak at 1027 cm\(^{-1}\) indicates the accumulation of sulfoxide groups at the interface. All these demonstrate that the key contributor to the formation of the interfacial films are Polar aromatic groups with long chains and not the highly condensed aromatic groups (Andersen et al., 2017).
The effect of sodium chloride. So far, we have discussed the systems of crude oil with DI water. However, subsurface oil reservoirs contain a variety of anions and cations, and the majority of them being sodium and chloride (Lager et al., 2007; Flanigan, 2000). We have performed both dilational and shear rheology measurements for 0.1 M solution of sodium chloride. Dilational rheology shows an evolution of the elastic modulus that is similar to that in the system with DI water, with a slightly lower final value by about 2 mN/m (Figure 3). By contrast, the onset of a measurable shear elastic modulus is significantly delayed, as shown in Figure 5. This suggests that the presence of salt has only a mild effect on the adsorption process (Figure 3 [A]), but it has a strong impact on the kinetics of molecular rearrangements giving rise to shear elasticity. Indeed, the presence of a cation in the aqueous phase facilitates the deprotonation and subsequent stabilization (energetically) of the polar species at the interface. The formation of acid salts at the interface might then hinder molecular aggregation and the establishment of a network through strong π-π bonds, favoring instead the formation of homogeneous films mostly dominated by weaker Van der Waals interactions.

The interfacial tension data for the system with sodium chloride solution shows an initial increase that proceeds for about 12 mins, followed by a decline similar to that in the case of DI water; this becomes more clear by looking at the data over a logarithmic scale of time (Figure 7).
Figure 7: The dynamic interfacial tension vs time on a logarithmic scale for crude oil against DI water and 0.1 M NaCl solution.

It is interesting to note that in the presence of NaCl, unlike DI water where we noticed a gradual decrease in the IFT, the IFT initially went up by about 5 mN/m, and then started falling gradually. Due to the presence of salts in the aqueous phase, the partition of organic phase – especially the polar species or short chain organic acids (< C12) – into the aqueous phase increases significantly. We hypothesize that when crude oil comes in contact with the aqueous phase the most polar species, short chain organic acids, start depositing at the interface first, and lower the initial interfacial tension relative to DI water. However, once these acids form salts with the NaCl in the aqueous phase, their solubility in the water increases, and they start partitioning into the aqueous phase that, as a consequence, creates void spaces in the interface resulting in a small increase of IFT. Once the higher chain polar groups starts accumulating at the interface, the IFT gradually starts going down. Overall, after 10 hrs, the NaCl solution lowers the IFT more than the DI water.

Conclusions

In this study, we have investigated the interfacial rheology of crude oil/water systems by combining shear and dilational rheology techniques. Interfacial tension is insufficient to characterize a system where surface-active species are present in crude oil, and insufficient to make decisions on production strategies and issues. We have shown that the interface between crude oil and water develops a complex viscoelastic response, characterized by a rapid development of dilational elastic modulus followed by a delayed onset of shear elasticity. We have proposed that such complex phenomenology originates from two distinct processes occurring at different timescales: surface-active molecules present in crude oil would first migrate to the interface, and then rearrange and associate to form system-spanning elastic networks with measurable shear modulus, an aging process that persists even after several days.

Chemical analysis of the interfacial film collected after the experiment indicates that the interface is indeed enriched with polar, surface-active species. To further test the impact of such polar molecules, we studied the properties of the interfacial film formed against salted water. The delayed onset of shear elasticity corroborates the hypothesis that molecular reorganization plays a vital role in the formation of the elastic film. The initial interfacial tension response for the system with sodium chloride shows a fast rise, followed by a slow drop in its value. We believe that this is due to smaller molecules that partition into the aqueous phase. We are currently extending this study to investigate the effect of different ionic species and different molarities of the aqueous phase on the interfacial rheology, interfacial tension response, and the chemical composition of the interfacial films.
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References


