Physical and chemical aspects of "precursor films" spreading on water from natural bitumen

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ABSTRACT

Interfacial chemistry and physics dominate fluid distribution within crude oil reservoirs and the efficiency of hydrocarbon recovery. For improvements to be made in extraction and production processes, it is essential that the complex boundaries between the different reservoir phases are better understood. The purpose of the present paper is to describe a multi-technique study of the spreading behavior and composition of so-called *precursor films* deriving from natural bitumen extracted from Athabasca oil sands at an air-water interface. Film spreading on deionized water and saline subphases was followed using ellipsometry and film pressure measurements. The films comprise surface-active bitumen components which could potentially influence the surface chemistry of the reservoir, with implications for mineral wettability, hydrocarbon recovery and the formation and stabilization of oil/water emulsions and oil foams during production. Infrared spectroscopy and mass spectrometry identified the presence of carbonyl groups as well as various classes of sulfur and oxygen hetero-species in the precursor films.

1. Introduction

Formed over millions of years, crude oil and gas reservoirs can be considered to exist under equilibrium or quasi-equilibrium conditions (Speight, 2007). However, when breached, by drilling for example, perturbations in pressure or temperature can cause fluid redistribution, with concomitant changes in the structure, composition and properties of interfacial regions present in the reservoir (Donaldson and Alam, 2008).

Thus, interfacial systems have been an important area of research for many years in order to understand the nature of both conventional and unconventional petroleum sources. Previous studies (Czarnecki et al., 2005; Gray et al., 2009; Jianjun et al., 2005; Wardlaw et al., 1991; Tweheyo et al., 1999; Denekas et al., 1959) have focused on aspects such as wettability (liquid-solid interfaces) and foam and emulsion formation and stabilization (gas-liquid and liquid-liquid interfaces, respectively), and how these relate to challenges associated with oil production. These phenomena will be determined by the composition of the reservoir, and the present study considers the nature and origin of certain surface-active species that could potentially influence the Gibbs energy of the various interfaces.

Here, we specifically concentrate on interfacial films that are produced from a natural bitumen by spreading on aqueous surfaces. Previously, such films have been termed "precursor films" as they are

the first films to appear on the surface when contacted with bitumen (Drelich and Miller, 1994; Drelich et al., 1995, 1996). It is likely that these films will contain the most surface-active species present in the bitumen, and herein we present results of a multi-technique approach concerned with their formation and chemical composition.

It is well-known that highly-purified mineral oils will not spread on water, preferring to remain in an equilibrium state on the surface as liquid lenses. However, as part of an extensive series of studies, Zisman found that spreading is promoted by the presence of surface-active solutes, such as organic acids and amines (Zisman, 1941). This is quantified in terms of the spreading coefficient, S_{OW}, attributed to Harkins and defined by the equation (Harkins and Feldman, 1922):

$$S_{OW} = \gamma_W - (\gamma_{OW} + \gamma_O) \tag{1}$$

in which the terms γ_W, γ_O and γ_{OW} are the respective air/water, air/oil and oil/water tensions. For highly-purified oils, equilibrium values are $\gamma_O \approx$ 20–25 mN/m and $\gamma_{OW} \approx$ 45–50 mN/m, such that S_{OW} is small, in the approximate range −2 to +8 mN/m, which represents a poor spreading condition. On the other hand, the presence of surface-active species in the oil phase causes a reduction in γ_{OW}, which according to eq. (1) leads to an increase in S_{OW}, thereby increasing the propensity for spreading. Thus, as Harkins deduced, for $S_{OW} > 0$, the oil phase spreads spontaneously until the water surface is covered, whereas if $S_{OW} < 0$, the oil forms a liquid lens.

The spreading of crude oils on water originates from the presence of polar surface-active components (Drelich et al., 1996) which produce an initial spreading coefficient that is positive (Drelich and Miller, 1994; Mani and Mohanty, 1997). By considering the polar (p) and dispersion (d) contributions to surface and interfacial tensions, Takamura et al. derived eq. (2) for the spreading coefficient (Takamura et al., 2012), from which the importance of the polarity of the oil phase is more evident from the middle term on the right-hand side of this equation. Thus, polar oils or oil components with significant polar surface tension contributions (γ_O^p) will increase the spreading coefficient.

$$S_{OW} = 2(\sqrt{\gamma_W^d \gamma_O^d} + \sqrt{\gamma_W^p \gamma_O^p} - \gamma_O) \qquad (2)$$

For conventional crude oils of relatively low viscosity, flow is driven by the positive spreading coefficients of the most polar molecules, and Marangoni coupling of the flow enables the whole oil to apparently spread spontaneously, with S_{OW} typically found to be $\sim$17–28 mN/m (Takamura et al., 2012) and sometimes significantly higher (Garrett and Barger, 1970). On the other hand, for more viscous heavy oils and bitumen, spreading of surface-active species by "edge diffusion" (Zisman, 1941) occurs more rapidly than the higher viscosity major components. This results in the latter components lagging behind the initial spreading front.

Drelich and colleagues were the first to recognize rapid-spreading bitumen "precursor films" at an air/water interface (formed from aqueous gas bubbles), when simulating the air flotation process widely used to remove bitumen from oil sands (Drelich and Miller, 1994; Drelich et al., 1995, 1996; Lelinski et al., 2004). As shown in Fig. 1, the spreading mechanism was suggested as comprising three stages (Lelinski et al., 2004): rapid surfactant molecular layer spreading over the clean air-water surface, followed by a slower, thicker precursor film, and finally, a very slow bitumen-rich layer that covers the surface. The authors also observed thickness variations in the precursor film layer, although these were not quantified. In addition, a yellow-brown film which preceded the bulk bitumen layer was also reported (Lelinski et al., 2004). Rainbow colors preceding the precursor films were explained in terms of additional components spreading ahead of the precursor film which were distinguishable by tensiometry (Lelinski et al., 2004). Measured film pressures ($\Pi_{pf} = \gamma_0 - \gamma$, where γ_0 is the surface tension of the clean aqueous surface and γ is the surface tension in the presence of the film) were found to be pH-dependent, being highest at the extremes of pH (Drelich et al., 1996). Within the pH range 3–9, however, a relatively modest surface tension reduction of $\sim$10–12 mN/m was observed (Drelich et al., 1996).

Lelinski et al. (2004) reported that activation energies for precursor film spreading over air bubbles ($\sim$66–123 kJ/mol, depending on the fractional bubble coverage) and for bulk bitumen viscous flow (80 kJ/mol) are similar in magnitude, suggesting that strong intermolecular forces contribute to each process. At ambient temperature, the precursor films initially spread on the air bubble surface with a velocity of $\sim$0.01–0.04 mm/s, whilst the bulk layer spreads more slowly,

$\sim$0.002–0.01 mm/s (Lelinski et al., 2004).

1.1. Composition of crude oil interfacial films

The accumulation of surface-active materials at aqueous crude oil interfaces has interested researchers for many years, primarily in an attempt to understand the formation and stability of water-in-oil emulsions (Blair, 1960). The interfacial films formed under these conditions are produced by different species present in the bulk oil diffusing to the water/oil interface. With time, larger molecules and solid particles are incorporated into the interface which consequently becomes increasingly more viscous (He et al., 2015; Mohammed et al., 1993).

The chemical composition of crude oils and natural bitumen includes larger hydrocarbon molecules, together with high concentrations of polar species. The polar fractions contain heteroatoms (predominantly sulfur, nitrogen, and oxygen) and heavy metals (primarily vanadium and nickel, and to a lesser extent iron and copper) (He et al., 2015). In a hydrocarbon environment, polar species contained in heavy fractions, such as asphaltenes and resins, will exhibit surface activity (Adams, 2014). Unsurprisingly, therefore, interfacial materials are enriched in polar species, and chemical analysis has identified numerous species classes, including carboxylic and hetero-acids (Andersen et al., 2016a). Such species are associated with operational problems, including corrosion, catalyst poisoning, deposit formation and emulsion stabilization (Andersen et al., 2016a), which has led to research into their isolation and characterization (Stanford et al., 2007; Wang et al., 2013). Isolated acid fractions (generically referred to as "naphthenic acids") frequently contain phenols but are principally complex mixtures of carboxylic acids (Speight, 2007).

Higher concentrations of certain naphthenic acids can sometimes result in the formation of naphthenate deposits in production pipelines through interactions with divalent metal ions, particularly Ca^{2+}, derived from produced or injection water. As suggested above, the species referred to as naphthenic acids vary from saturated acyclic or alicyclic compounds to aromatic and polyaromatic components (Mapolelo et al., 2009, 2011). Mapolelo et al. found differences in negative-ion ESI FT-ICR-MS between deposited naphthenic acids and species isolated from crude oil emulsions (Mapolelo et al., 2009). Calcium naphthenate deposits were found to contain the O8 class C_{80} naphthenic acid structure known as "ARN acid" (Mapolelo et al., 2009; Headley et al., 2016). On the other hand, sodium naphthenate-stabilized emulsions fall into the O2 class (Mapolelo et al., 2009). (Species classes in the present paper are designated by heteroatom content using the notation NxOySz, where x, y and z are integers representing the respective numbers of the particular heteroatom in each molecule.)

Our current interest focuses on the physicochemical aspects of precursor films, including their chemical composition. Here, we use different experimental techniques to investigate precursor films formed from a sample of Athabasca bitumen. The physical characteristics studied include surface activity, spreading thickness and wetting
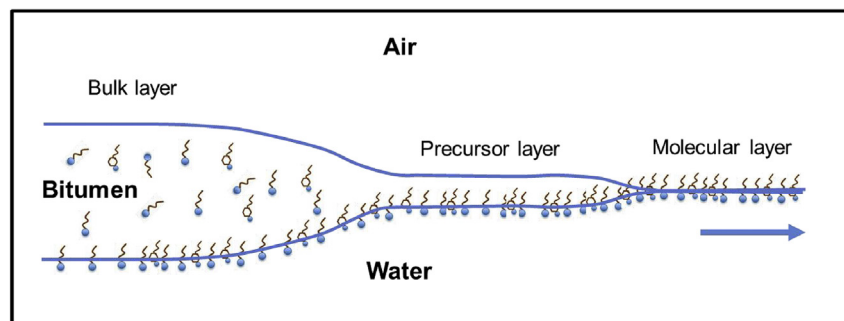

Fig. 1. Bitumen spreading and precursor film formation at a water/air interface, after Lelinski et al. (Lelinski et al., 2004).