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 [1]. 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 [2].

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 [3-8] 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 [9-11]. 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 [12]. This is quantified in terms of the spreading coefficient, S_{OW} , attributed to Harkins and defined by the equation [13]:

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

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 $\gamma_O \approx 20\text{-}25$ mN/m and $\gamma_{OW} \approx 45\text{-}50$ 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 [11] which produce an initial spreading coefficient that is positive [9,14]. By considering the polar (p) and dispersion (d) contributions to surface and interfacial tensions, Takamura et al. derived eq. 2 for the spreading coefficient [15], 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.

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

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 $\sim 17\text{-}28$ mN/m [15] and

sometimes significantly higher [16]. On the other hand, for more viscous heavy oils and bitumen, spreading of surface-active species by “edge diffusion” [12] 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 [9-11,17]. As shown in Fig. 1, the spreading mechanism was suggested as comprising three stages [17]: 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 [17]. Rainbow colors preceding the precursor films were explained in terms of additional components spreading ahead of the precursor film which were distinguishable by tensiometry [17]. 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 [11]. Within the pH range 3-9, however, a relatively modest surface tension reduction of ~10-12 mN/m was observed [11].

Lelinski et al. [17] reported that activation energies for precursor film spreading over air bubbles (~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 ~0.01-0.04 mm/s, whilst the bulk layer spreads more slowly, ~0.002-0.01 mm/s [17].

Figure 1. Bitumen spreading and precursor film formation at a water/air interface, after Lelinski et al. [17].

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 [18]. 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 [19,20].

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) [19]. In a hydrocarbon environment, polar species contained in heavy fractions, such as asphaltenes and resins, will exhibit surface activity [21]. Unsurprisingly, therefore, interfacial materials are enriched in polar species, and chemical analysis has identified numerous species classes, including carboxylic and hetero-acids [22]. Such species are associated with operational problems, including corrosion, catalyst poisoning, deposit formation and emulsion stabilization [22],

which has led to research into their isolation and characterization [23,24]. Isolated acid fractions (generically referred to as “naphthenic acids”) frequently contain phenols but are principally complex mixtures of carboxylic acids [1].

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 [25,26]. Mapelo *et al.* found differences in negative-ion ESI FT-ICR-MS between deposited naphthenic acids and species isolated from crude oil emulsions [26]. Calcium naphthenate deposits were found to contain the O8 class C_{80} naphthenic acid structure known as “ARN acid” [26,27]. On the other hand, sodium naphthenate-stabilized emulsions fall into the O2 class [26]. (Species classes in the present paper are designated by heteroatom content using the notation $\text{N}_x\text{O}_y\text{S}_z$, 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 properties. This is complemented by chemical characterization of the isolated film material to provide some insight into species classes responsible for the physical characteristics.

2. Experimental section

2.1. Materials

A sample of Athabasca bitumen produced using steam-assisted gravity drainage (SAGD) was used as received. Table 1 contains some relevant inspection data for the sample.

Table 1. Inspection data for the bitumen used in this study (as provided by the supplier unless otherwise indicated).

Property	
Density (15 °C), g/mL	1.012
API gravity, degrees	8.2
Viscosity (60 °C), cSt	2750
Pentane-insoluble asphaltenes, % w/w	16.1
Water content, ppm by Karl-Fischer titration	55*
Salt content, g/m ³ by ASTM D3230	79*
Total acid number, mg KOH/g	3.0
%C	83.33*
%H	10.84*
%N	0.42*
%S	5.43

*Determined in the authors' laboratory using standard techniques.

All reagents were used as received from Sigma-Aldrich Ltd. The solvents were of spectrophotometric grade. Deionized water was from a Millipore Direct-Q system, and silicon wafers were from Wacker-Chemitronic GmbH, Germany.

2.2. Precursor film formation and physical characterization

Bitumen spreading can be demonstrated by placing a small quantity of bitumen (~0.5 g) in a glass beaker and rapidly covering it with deionized water (Fig. 2). At this stage no visible evidence of an oil film on the water surface is apparent, indicating that oil components are not readily transferred through the water phase itself. However, removal of some of the water to expose the upper surface of the bitumen to create a bitumen/water/air triple junction causes a thin oil film to spread rapidly over the water surface (in accord with eq. 1). This is the precursor film, which is accompanied by a thicker bitumen-rich film which spreads more slowly as largely as described by Lelinski et al. [17] and depicted in Fig. 1. This procedure, or minor variations thereof, was used to isolate material for specific analyses as will be described below.

Figure 2. A bitumen drop totally covered with water shows no sign of spreading (left), whereas when the water surface is lowered, the bitumen starts to spread when partially covered with water (middle – side view and right - top view).

2.2.1. Monitoring precursor film spreading using ellipsometry

The spreading of bitumen components on the surface of water or saline solutions was followed using ellipsometry, which is a sensitive, non-intrusive optical analysis technique for studying surfaces and interfaces through the reflection of light [28,29]. Briefly, a linearly-polarized light beam becomes elliptically polarized upon reflection, as the light components are reflected differently when parallel (p) and perpendicular (s) to the plane of incidence. Ellipsometry is

used to determine the ratio (known as the ellipticity, ρ) of the complex reflection coefficients, R_p and R_s , given by the standard ellipsometry equation [28]:

$$\rho = \frac{R_p}{R_s} = \tan \Psi \exp(i\Delta) \quad (3)$$

where $\tan \Psi$ is the amplitude ratio of the reflected beam components (r_p/r_s) and Δ is the phase difference ($\delta_p - \delta_s$) between the p and s components. By solving eq. 3, based on an air/film/substrate slab model, ellipsometry enables the determination of the complex refractive index ($N = n - ik$) components, the refractive index (n_s) and absorption coefficient (k_s) of the substrate (the aqueous subphase in this case), and the thickness (h) and refractive index (n_f) of the film, which is assumed to be thin enough to be non-absorbing ($k_f = 0$). The refractive index of air, n_0 , is taken to be 1.000.

In this study, a Plasmos SD2000 rotating analyzer ellipsometer with a HeNe laser (wavelength = 632.8 nm) and ~20 μm microspot optics was used to determine the ellipsometric parameters Ψ and Δ . The system software then calculates the surface film thickness based on the above-described model and baseline parameters for the clean aqueous surface. Uncertainties in the thickness measurements resulting from fluctuations in the baseline n_s and k_s parameters are estimated to be ± 3 nm under the present conditions.

A small quantity of bitumen (~0.1 g) was applied to the tip of a glass rod. At the initiation of the experiment, the immobilized bitumen was positioned to make partial contact at the center point of an aqueous surface (depth ~5 mm) contained in a clean Petri dish (10 cm diameter), as shown in Fig. 3. The precursor film then radiated from the bitumen, with the film thickness at the laser spot position being continuously monitored. During the course of the experiments, the film was not observed to extend and adhere to the walls of the Petri dish.

Figure 3. An immobilized sample of bitumen supported by a glass rod making contact with an air/water surface. The central light circular area is the formed precursor film. The position relative to the laser spot on the aqueous surface is also shown.

2.2.2. Aqueous surface pressure determination in the presence of precursor films

The Wilhelmy plate technique (Krüss K10 surface tensiometer) was used to determine the change in surface tension of aqueous substrates as a function of time during precursor film spreading. For these measurements, the aqueous phases were contained in a Petri dish (diameter = 15 cm) with the Pt-Ir Wilhelmy plate (perimeter = 4 cm) positioned 25 mm from the center of the dish where the bitumen drop was contacted, i.e., an equivalent position as used for the ellipsometry experiments in Fig. 3. The reduction in surface tension from the initial values of 72.0-73.2 mN/m (for deionized water and the saline solutions, respectively) was measured continuously during precursor film spreading at the ambient temperature of $23 \pm 2^\circ\text{C}$. For comparison with the film thickness measurements, the pH of the solutions was not adjusted from their natural values in deionized water (in the range 5.9 ± 0.3), which lie in a constant film pressure region (extending from pH ~3-9) as previously observed by Drelich et al. [11]. Uncertainties in the measured surface tension values were estimated to be ± 0.2 mN/m.

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209 *2.2.3. Preparation and characterization of supported films*

210 Bitumen precursor films were transferred from the aqueous surface to clean (acetone and water-
211 washed) standard glass microscope slides or silicon wafers. This involved manually
212 withdrawing the partially pre-immersed solid substrates through the water surface containing
213 the precursor film, which were then allowed to drain vertically and dry in air. As with
214 Langmuir-Blodgett film deposition, preparing the film in this way should ensure that the
215 water/film interface becomes a solid/film interface, with the configuration of the original
216 film/air surface being retained. For contact angle studies, three separate glass slides were
217 prepared from successive withdrawals from a single surface film.

218 The silicon wafer-supported films were imaged with an Olympus DXS500 Opto-Digital 3D
219 microscope prior to AFM imaging. Polarized light microscopy was primarily used because of
220 the strong color response in the presence of thin films [30,31]. The films were then imaged
221 using a Bruker diInnova atomic force microscope in tapping mode (256 lines and a scan rate
222 of 4 Hz). The images were post-processed using Bruker NanoScope Analysis 1.5 software.

223 Advancing and receding contact angle measurements were made by applying deionized water
224 drops to different positions on the coated microscope slides via a syringe needle. Sessile drop
225 images were taken using a model 1000B drop shape analyzer (First Ten Ångströms Inc.,
226 Portsmouth, VA, USA) on both sides of each drop for each of the slides, and from three
227 different positions on the surface in order to obtain average values.

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2.3. *Chemical characterization of precursor films*

For the chemical characterization tests, sufficient precursor film sample (~10-15 mg) was accumulated from several spread films obtained from fresh bitumen drops as described in section 2.2.3.

2.3.1. *Infrared spectroscopy*

Infrared spectra of bitumen and precursor film material obtained by sweeping the surface with clean glass cover slips were determined in attenuated total reflection (ATR) mode using an Alpha FTIR spectrometer (Bruker UK, Banner Lane Coventry). Small volumes of sample dissolved in chloroform were placed on the ATR crystal and the spectra recorded after solvent evaporation.

2.3.2. *Time-of-flight secondary ion mass spectrometry (TOF-SIMS)*

Samples of isolated precursor film were mounted and analyzed in an IONTOF V TOF-SIMS 5 spectrometer (IONTOF GmbH, Münster, Germany). Positive and negative SIMS spectra were acquired in the mass range 1-300 *u*. Static SIMS (ion dose $<1 \times 10^{13}$ ions cm^{-2}) used a 25 keV Bi_3^+ primary ion beam, 9.5 keV extractor voltage, over an area of $100 \times 100 \mu\text{m}^2$. Spectra were acquired and processed using the manufacturer's software.

2.3.3. *High-resolution mass spectrometry (HRMS)*

High resolution mass spectra of isolated precursor films were generated using a Thermo Orbitrap high resolution mass spectrometer (Thermo Scientific, NJ, USA) operating in positive or negative electrospray ionization (ESI) modes. MS tune, XCalibur and Chromeleon software were used to control the instrument. The samples of interest were dissolved in a toluene-methanol (60:40 v/v) solvent mixture at a concentration of 0.3 mg/mL. Ammonium hydroxide (0.1 wt%) was added for negative ESI measurements, (-)ESI, and formic acid (0.1 wt%) was

added for positive ESI, (+)ESI. Obvious contaminant peaks were manually removed from the spectra during processing.

3. Results

3.1. Precursor film spreading at bitumen/water/air contact regions

As described above, precursor film spreading was only observed during air/water/bitumen three-phase contact; no visual evidence of component leaching of water-soluble materials from completely submersed bitumen in water was seen (Fig. 1). Once formed, the precursor films were easily transferred from the aqueous surface to solid glass or silicon substrates by manual dipping/retraction, enabling further characterization by optical microscopy, AFM imaging and water contact angle determinations.

Thus, in Fig. 4(a) is shown a polarized light image of the precursor film picked up on a silicon wafer surface. This particular image illustrates the thickness variation seen in films transferred by contact with the solid surface. Evidence of film stacking and drainage can be seen from the range of colors, as well as the presence of inclusions within the film which are possibly due to water droplets or small clay particles, both of which may be present in extracted heavy oils. The region designated as ‘i’ is closely associated with a “ridge” formed by overlapping two film layers, whereas region ‘ii’ contains a thicker built-up film. AFM images from these two regions are shown in Fig. 4(b) in which the topography of the upper surfaces of the films transferred to the silicon wafer substrate can be seen.. The NanoScope software analysis reported *z*-ranges for regions ‘i’ and ‘ii’ of 3.47 and 7.97 nm, respectively, indicating that the former is smoother than the latter.

3.2. *Monitoring precursor film spreading using ellipsometry*

Ellipsometry provides a very effective means of detecting the presence of surface films [29]. Initially the aqueous substrate baseline optical parameters n_s and k_s (substrate refractive index and absorption coefficient, respectively) were determined, with the film refractive index (n_2) and n_0 set at 1.450 and 1.000, respectively. The n_2 value used is an average value representative of a range of polar organic molecules [32,33]. However, it is expedient to use this value to enable efficient calculations to be made by the proprietary instrument software assuming a 'slab' layer model for the air/film/substrate system, in which the only unknown parameter is the organic film thickness [34].

With reference to Fig. 3, the laser spot is positioned ~25 mm from the center of the Petri dish at which point a supported bitumen drop is placed in contact with the aqueous surface. The film spreads radially from this central contact position and as the spreading front passes the laser 'interrogation' position, film thickness measurements were made at approximately 1 s intervals.

The resulting spreading profiles for deionized water, 30,000 mg/L sodium chloride and 30,000 mg/L calcium chloride solutions all follow similar general features, as shown in Fig. 5.

Figure 4. (a) Heterogeneity of an isolated precursor film supported on a silicon wafer shown by thickness variations highlighted in a polarized light image. The marked regions ‘i’ and ‘ii’ refer to the approximate positions at which AFM images were acquired. (b) AFM topographical images (scan size = $0.2\ \mu\text{m} \times 0.2\ \mu\text{m}$) of different regions of the silicon wafer-supported precursor films.

Thus, the profiles show initial induction times (indicated as t_i in inset to Fig. 5(a)) of ~ 20 - 50 s before any film components reach the laser spot. During this time the measured thickness

remains at a background level of $\sim 2\text{-}3$ nm, which provides an indication of the uncertainty in the film thickness determinations resulting from variations in the n_s and k_s baseline parameters, as indicated earlier. This period is followed by a sudden increase in film thickness to $h_i \sim 30\text{-}50$ nm, which is very close to the y-axis in Fig. 5 but can be seen more clearly in the inset to Fig. 5(a), as the first spreading components reach the laser spot; this thickness is maintained for several seconds in the case of deionized water but appears to be slightly shorter and consequently less obvious for the saline solutions (Figs. 5(b) and 5(c)). The profiles then show a slower, steady increase in film thickness over approximately ten minutes, by which time the film thickness approaches a maximum value (h_{max}) of $\sim 150\text{-}200$ nm. Thereafter, the film thickness becomes increasingly erratic, which we suggest is a consequence of film dilution and break-up as the supply of surface-active components from the bitumen drop becomes depleted, leading to non-uniformity of the film structure as will be discussed below.

After the initial jump to h_i at time t_i (see insets in Fig. 5) the subsequent film thickness is found to scale with time according to the power law

$$h_t \propto (t - t_i)^\alpha \quad (4)$$

up to the maximum value, h_{max} . In eq. 4, h_t is the film thicknesses at time t , and α has a value of 0.46 for water determined by non-linear least squares regression analysis. In the case of the sodium chloride subphase, the data points do not allow a satisfactory exponent value to be obtained. For the calcium chloride subphase α is 0.35.

To the best of the authors' knowledge, the thickness development of such films according to eq. 4 has not been previously reported. However, unlike in the present case where a viscous oil reservoir of surface-active species is effectively anchored at the aqueous surface, some workers have studied the spreading of small liquid drops, and monitored the spreading drop radius as a

330 function of time. Thus, van Nierop et al. [35] used drops of mineral oil containing low
331 concentrations of oleic acid, for which the scaling exponent of the radius with time was reported
332 to be $0.64 < \alpha < 0.89$. In the case of a surfactant-laden drop spreading on a thin film, where
333 the drop acts as a source of constant concentration, the radius of the spreading film has also
334 been shown to scale as $t^{0.5}$ [36].

Figure 5. Ellipsometric film thickness profiles for bitumen spreading on (a) deionized water; (b) 30,000 mg/L aqueous NaCl; and (c) 30,000 mg/L aqueous CaCl₂. The insets show data on a logarithmic time axes to accentuate the early stages in the profiles.

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341 3.3. Surface tension (and film pressure) measurements

342 Drelich et al. used surface tension measurements to characterize the surface activity of
 343 precursor films derived from Whiterocks bitumen diluted with 10% kerosene [9]. pH was found
 344 to influence the film pressure, with Π_{pf} increasing significantly at the extremes of pH, while
 345 remaining near-constant at ~ 15 mN/m in the pH range 3-9. This suggests that the precursor
 346 film contains both acidic and basic components, the ionized forms of which result in higher Π_{pf}
 347 values.

348

349 **Figure 6.** Film pressure profiles for bitumen spreading on deionized water (circles), 30,000 mg/L NaCl (squares)
 350 and 30,000 mg/L CaCl₂ (triangles).

351 As found for the ellipsometric film thicknesses, different regions can also be distinguished in
 352 the precursor film pressure profiles for the aqueous subphases shown in Fig. 6. In this case, the
 353 data can be fitted using eq. 5, which contains two sets of weighted exponentials comprising

rate constants (r) and film pressure components (Π). As for the ellipsometric profiles above, t_i represents the time taken for the film to reach the point of measurement.

$$\Pi_{pf}^t = \Pi_{pf}^{max} - \Pi_1 \exp(-r_1(t - t_i)) - \Pi_2 \exp(-r_2(t - t_i)) \quad (5)$$

Table 2. Fitting parameters for the film pressure profiles shown in Fig. 6.

Aqueous subphase	Π_{max}	Π_1	Π_2	t_i	r_1	r_2
	(mN/m)			(s)	(s ⁻¹)	
Deionized water	12.9	7.63	5.27	30	1.80×10^{-2}	1.45×10^{-3}
30,000 mg/L NaCl	15.6	8.57	7.03	50	2.01×10^{-2}	1.09×10^{-3}
30,000 mg/L CaCl ₂	14.9	7.37	7.53	30	5.99×10^{-2}	2.91×10^{-3}

Analysis of the data extracted from Fig. 6, shown in Table 2, indicates that there is a fast initial stage (Π_1 , r_1) during which the film pressure shows a rapid increase, followed by a slower second stage (Π_2 , r_2), possibly involving components of lower surface activity or interfacial rearrangement, which is approximately an order of magnitude slower for each subphase. As discussed above, there are likely to be numerous individual components contributing to the spreading film, but it is also reasonable to expect that these might fall within a smaller number of classes based on similar spreading rates (driven by their respective surface activities). The stages for each of the aqueous subphases are characterized by $\Pi_1 \approx \Pi_2$ with some subphase dependence. Spreading on deionized water produces the lowest maximum film pressure. Interestingly, the fastest spreading, as seen in the film pressure measurements, occurred on the CaCl₂ subphase. Calcium ions are known to interact with crude oil components, in particular carboxylic (i.e., naphthenic) acids [37,38], and the observation of higher spreading rates may signify their presence in the interfacial film. Given the experimental differences mentioned

above, the induction times preceding the increase in film pressure are similar to those seen in Fig. 5 for the corresponding ellipsometric responses.

Comparing Figs. 5 and 6 it is evident that the ellipsometry and film pressure profiles follow similar behavior during the early film development up to the maximum film thickness, where the film pressure reaches ~ 12 mN/m for a precursor film thickness of ~ 150 - 180 nm. Thereafter, as observed above, the ellipsometric behavior becomes more erratic, whereas the film pressure continues to increase, albeit more slowly. The interpretation based on these experimental approaches may therefore suggest that if slower spreading components are responsible for the second stage, as discussed above, this may also involve some film disruption and reorganization which in the case of the ellipsometric measurements leads to somewhat erratic behavior. In reality, however, several stages may actually be involved which appear to fall conveniently within our “fast” and “slow” stages.

3.4. *Spreading coefficients of diluted bitumen on water*

As a comparison with the foregoing, surface and interfacial tensions for bitumen diluted with toluene were measured and are summarized in Table 3 together with calculated spreading coefficients based on eq. 1. From these data, the spreading coefficient for the whole oil can be estimated to be 24.6 ± 1.0 mN/m by extrapolation of the $\gamma_{oil/air}$ and $\gamma_{water/oil}$ values on a logarithmic %bitumen axis to 100% bitumen, giving the respective values 29.7 and 17.2 mN/m. The large positive spreading coefficient underlines the predisposition of bulk bitumen to spread on a water surface, albeit substantially inhibited by the high viscosity as discussed above.

Table 3. Surface and interfacial tensions and calculated spreading coefficients for bitumen solutions in toluene determined by the du Noüy ring method.

Bitumen concentration in toluene (wt%)	$\gamma_{oil/air}$	$\gamma_{water/oil}$	$S_{oil/water}^*$
	(mN/m)		
0	28.2	34.0	9.4
0.5	29.2	24.0	18.3
1	29.0	22.0	20.0
10	29.1	19.9	20.7
50	29.8	18.1	23.6

* $\gamma_{water/air} = 71.5$ mN/m.

3.5. Physico-chemical and mass spectrometric analyses of isolated precursor films

3.5.1. Contact angle measurements

Fig. 7 summarizes the mean advancing (θ_a) and receding (θ_r) contact angles for water on the successively withdrawn films transferred to glass microscope slides. No time-dependency was observed in the advancing contact angle measurements resulting from spreading of the film over the water drops, thus indicating that the transferred film remains intact on the solid support during the experimental timescale (minutes). The observed trends are consistent with decreasing film thicknesses for the successive transfers. The first transfer produces the most hydrophobic glass surface, characterized by $\theta_a \approx 90^\circ$, with the subsequent transfers yielding lower θ_a values of $\sim 55^\circ$. These values reflect increasing contributions from the hydrophilic glass substrate, which are also evident in the decreasing θ_r values.

Figure 7. Advancing and receding contact angles for deionized water drops placed on successively withdrawn (1, 2 and 3) precursor films transferred to glass microscope slides.

3.5.2. Infrared spectroscopic analysis

To the best of our knowledge, the chemical characterization of precursor films produced from bitumen as discussed above has not previously been described. Compared to most conventional crude oils, heavy crude oils and bitumen are rich in sulfur, nitrogen and oxygen hetero-species, and even with increasing developments in high resolution mass spectrometry (HRMS), the precise identification of the individual compounds responsible for the precursor films described above remains highly challenging. For this reason, we describe herein an attempt to identify the general chemical nature of species comprising the precursor films using infrared spectroscopy, time-of-flight secondary ion mass spectrometry (ToF-SIMS) and HRMS.

Thus, Fig. 8(a) compares the infrared spectra for the Athabasca bitumen sample, the precursor film, and the *n*-heptane maltene and asphaltene fractions, while Fig. 8(b) emphasizes the differences in the baseline-normalized difference spectrum of the precursor film. Although infrared spectra of crude oil and its components only provide limited structural information,

they are similar to those reported elsewhere [39]. From Fig. 8(a), the precursor film spectrum has features also evident in the maltenes and asphaltene spectra, which can be identified in most crude oils. In particular, the precursor film infrared spectrum contains: (i) an enhanced C=O vibrational band at 1700-1725 cm^{-1} , possibly due to carboxylic acids [40], which is present at a lower level in the spectrum of the *n*-heptane maltenes spectrum, but absent in the corresponding asphaltene spectrum, suggesting that asphaltene is not for a major contributor to the precursor film; (ii) an enhanced band at 1600 cm^{-1} , assigned to C=C stretching modes, which suggests higher aromatic character than the maltenes [41]; (iii) a stronger sulfoxide (S=O) band than seen in maltenes and asphaltenes fractions at 1030 cm^{-1} [15]; and (iv) a small, broad O-H band at $\sim 3300 \text{ cm}^{-1}$ (which could be due to water). Other bands in the 700-1000 cm^{-1} region can be attributed to aromatic vibration modes. Strong absorption bands around 720 cm^{-1} and weaker bands around 900 cm^{-1} are also observed in the other spectra to varying degrees (Fig. 8(a)) and have been attributed to C-H out-of-plane bending vibrations [40].

The appearance of the above features in the precursor film spectrum is not surprising, as they are common functional groups known to confer surface activity to organic molecules [41]. However, since infrared spectra provide relatively limited structural information, we also subjected the precursor film material to mass spectrometry analysis, both time-of-flight secondary ion mass spectrometry (ToF-SIMS) and electrospray ionization high-resolution mass spectrometry (ESI HRMS).

Figure 8. (a) Infrared transmittance (T) spectra of the precursor film material, the original bitumen, and n -heptane maltene and asphaltene fractions; and (b) the (precursor film spectrum – bitumen spectrum) difference transmittance (ΔT) spectrum. The vertical dashed lines in (a) highlight the main spectral differences, which are accentuated and assigned in (b). Bands marked with asterisks are due to methyl and methylene C-H stretching and bending vibration modes. The circled bands indicate the greatest differences in the precursor film spectrum.

3.5.3. Time-of-Flight SIMS analysis

Fig. 9 shows positive and negative ToF-SIMS spectra for the isolated precursor film. Below 80 u , the positive ToF-SIMS spectra contain a number of peaks assignable to the homologous aliphatic hydrocarbon fragments $C_nH_{2n+1}^+$, $C_nH_{2n-1}^+$ and $C_nH_{2n-3}^+$. Na^+ and K^+ ions are also indicated at 23 u and 39 u (very small), respectively, although the absence of Cl^- in the corresponding negative ion spectrum suggests that these are associated with the precursor film and not due to residual salinity in the bitumen sample. Various oxygen-containing ions, such

as CHO^+ , C_2HO^+ , $\text{C}_2\text{H}_3\text{O}^+$, $\text{C}_3\text{H}_3\text{O}^+$, $\text{C}_3\text{H}_5\text{O}^+$, $\text{C}_4\text{H}_3\text{O}^+$, $\text{C}_4\text{H}_7\text{O}^+$, $\text{C}_5\text{H}_5\text{O}^+$, and $\text{C}_5\text{H}_7\text{O}^+$ are also indicated in the positive spectra. Some homologous aromatic ions are evident, as indicated in Fig. 9(a) for the early members of the series $\text{C}_6\text{H}_5^+ + n\text{CH}_2 = 77, 91, 105, \text{ and } 119$. We speculate that evidence of carboxylic acids arises from pairs of ions corresponding to RCO_2H_2^+ and RCO^+ (with a difference in m/z of 18), as reported for lauric acid [42]. Possible pairs of simple species fitting this pattern are seen at m/z 115/97 (cyclopentanoic acid, mw 114 u) and species corresponding to the indicated pairs of ions in Fig. 9(a). The negative ToF-SIMS spectra contain oxygen-, carbon- and sulfur-based ions, examples of which are included in Fig. 9(b). As shown, there is evidence for the possible presence of thiolate (HS^-) and other sulfur species C_2HS^- , S_2^- or SO_2^- , SO_3^- and SO_3H^- . One literature report of a SIMS analysis of a bitumen interfacial extract showed the presence of sodium naphthenates and aliphatic and aromatic hydrocarbons fragments [43].

Figure 9. Precursor film ToF-SIMS spectra: (a) positive, and (b) negative ions. Note the different vertical axis scales, and that some of the assignments may be speculative (see text). The labels a-a', b-b', c-c' and d-d' represent tentatively-assigned carboxylic acid species pairs RCO_2H_2^+ and RCO^+ , as discussed in the text.

3.5.4. High Resolution Mass Spectrometry (HRMS)

HRMS is a highly effective method for the detection and identification of polar compounds (primarily containing sulfur, oxygen and nitrogen) in crude oil and crude oil fractions [23]. In the present work, electrospray ionization (ESI) mass spectrometry, in positive and negative modes (i.e., (+)ESI and (-)ESI), has been used to provide an indication of heteroatomic class species in the precursor film compared with the original bitumen. (-)ESI is able to detect phenols, naphthenic acids, and neutral nitrogen compounds without pre-fractionation [24,43], whereas (+)ESI is able to detect basic nitrogen (e.g., pyridine homologs) [24,44].

Fig. 10 highlights comparative acidic and basic heteroatom classes for the isolated precursor film and the original bitumen, with only the species that are present at >1% relative abundance in the samples being shown. In particular, it is apparent that the film contains significant levels of oxidized sulfur species, as well as being enriched in O3 and O4 classes (i.e., molecules containing three and four oxygen atoms, respectively), whereas N1, N1S1 and O1 classes are depleted in the film. The increased relative abundance of the more polar species in the film is consistent with expectation, based on anticipated surface activity leading to more rapid surface fractionation of molecules in these classes. It is also seen that O2 species, most likely due to carboxylic acids [27] and consistent with the infrared spectrum (Fig. 8(a)), constitute the major hetero-species present in both the bitumen and the film. On the other hand, Fig. 10(b) indicates similar features in the (+)ESI spectra, in which depletion of N1, N1S1 and O1 classes is again seen in the film, together with enrichment of oxidized sulfur species.

Figure 10. Relative abundances of heteroatom classes from (a) (+)ESI and (b) (-)ESI HRMS analysis of the precursor film (blue) and bulk oil (red).

Generally, it is seen that hetero-species present in the original bitumen are also found in the precursor film albeit to different extents. Thus, it is evident from the comparisons given in Fig. 10 that nitrogen species are generally depleted in the precursor film, which is also consistent with asphaltenes also being largely absent from the precursor film, whereas oxygen and oxygen/sulfur classes are generally more abundant.

Although not unequivocal, HRMS ESI analysis can provide directional indications of the relative abundances of specific species within classes, although without additional HRMS information, cannot necessarily furnish absolute quantification by itself [27]. Therefore, a comparison of specific N1 species in (+)ESI and (-)ESI spectra is shown in Fig. 11 as DBE (double-bond equivalent, DBE; for a molecule with the formula $C_cH_hN_n$, $DBE = c - h/2 + n/2 + 1$) vs. carbon number distributions. From these data it is evident that the distribution of these species remains very similar to the original bitumen, although somewhat depleted in the precursor film. The relative size of the spots in the bubble plots indicates the concentration of species with a given DBE and carbon number, and Fig. 11 therefore illustrates the comparative abundance of pyridines and indoles, as identified in the ESI spectra, with the former being more abundant.

Figure 11. Iso-abundance plots of DBE vs. carbon number showing N1 class species in bitumen (left) and its precursor film (right) for (a) (+)ESI (e.g., pyridines), and (b) (-)ESI (e.g., indoles, carbazoles).

521 In Fig. 12(a), the O2 class species, as identified in the (-)ESI analysis, are seen to be relatively
522 equally distributed in the bulk bitumen and precursor film. As mentioned above, these may be
523 largely expected to be carboxylic acids, with the (-)ESI analysis identifying species with $1 <$
524 $\text{DBE} < 6$ and carbon numbers $\text{C}_{10} - \text{C}_{32}$ in both the bitumen and precursor film, indicating the
525 efficient general transfer of species in this class from the bitumen to the spreading film. The
526 results in Fig. 12(a) suggest that O2 species in the precursor film may be centered on slightly
527 lower DBE and carbon number, possibly signifying more fatty acid components ($\text{DBE} = 1$).
528 The presence of acid species in the precursor film is consistent with their surface activity and
529 slight water solubility, these features being responsible for the accumulation of naphthenic
530 acids in wastewater generated, for example, during oil sands processing [45]. On the other
531 hand, in the (+)ESI analysis, other O2 species (e.g., esters) were found to be enriched in the
532 film. However, contributions from this class in the original bitumen were $<0.5\%$, and therefore
533 below the reporting level in this study, whereas much higher concentrations were detected in
534 the film, in the range $1 < \text{DBE} < 14$ and carbon numbers $\text{C}_8 - \text{C}_{30}$. Owing to their unlikely
535 presence in native bitumen, this could suggest that such species have arisen through oxidation
536 occurring during formation and processing of the film.

Figure 12. Iso-abundance plots of DBE vs. carbon number showing O2 class species in bitumen (left) and its precursor film (right) for (a) (-)ESI and (b) (+)ESI. In (b), O2 class species in bitumen were detected at <0.5% and therefore below the significant reporting level.

An observation based on the data in Fig. 10 is that the more oxidized oxygen and oxygen/sulfur classes are generally enriched in the precursor film compared with the original bitumen. It is possible that enrichment could be in part due to aerial oxidation during film formation, although not all oxidized sulfur species are more abundant in the film. Under (-)ESI conditions, for example, it appears from Fig. 10 that the O2S1 class is relatively depleted in the film. This class includes, *inter alia*, sulfones, consistent with the infrared spectral data mentioned earlier with respect to Fig. 8. Thus, Fig. 13 shows a comparison between components in the bitumen and precursor film for the O2S1 class, from which there are considerable quantitative differences between the respective bitumen and film components. In particular, the narrower

range of O2S1 species in the film compared with the parent bitumen indicates that only a fraction of this class is incorporated into the film, with $3 < \text{DBE} < 8$ and carbon number C_{18} - C_{30} species remaining more abundant in the bitumen. It is unclear why this might be the case, since there appears to be little overall specificity from within this class with respect to incorporation into the film. It may be the case that these species, possibly in common with many others, may be adventitiously present as a result of association with other, more surface-active species.

Figure 13. Iso-abundance plots of DBE vs. carbon number showing O2S1 class species in (a) bitumen and (b) its precursor film (right) for (-)ESI.

Other species distributions are provided as Supplementary Material (Figs. S1-S4) showing O1, O1S1, O3S1, O4S1, O3 and O4 class distributions. The most abundant species in the O3S1 and O4S1 classes have $1 < \text{DBE} < 8$ and carbon numbers C_{15} - C_{32} . O1S1 species (possibly sulfoxides) in the parent oil and the precursor film have similar unsaturation levels, while those in the precursor film have longer or more side chains, which increases the carbon number.

Our reason for describing the composition of certain species classes is to emphasize the complexity of bitumen and the derived films, which should never be underestimated. To

provide a degree of perspective, Qian et al. [46] identified some 3000 individual species in a South American heavy oil with carbon numbers C_{15} - C_{55} contained in alicyclic and aromatic ring structures within the O2, O3, O4, O2S1, O3S1 and O4S1 classes alone. However, the results presented herein provide a comparative guide to components present in the precursor film, which will be considered further below.

4. Discussion

In the early 1940s, Zisman [12] showed that the spreading of mineral oils over a water surface can arise through the presence of certain surface-active molecules, making it of interest to understand within the context of crude oil chemistry. Subsequently, Drelich and coworkers identified the formation of spreading films upon contacting natural oil sands (Whiterocks, UT, USA) bitumen with an air/water interface [9-11,17]. In this context, the term *precursor film* serves to indicate a film formed which precedes the spreading of the major bitumen (or crude oil) components of lower surface activity.

Thus, in the present work we sought to confirm the nature of surface-active components in a sample of Athabasca bitumen, and determine aspects of their spreading behavior on neutral aqueous subphases. In this way, we aimed to confirm the findings made by Drelich's group, and extend their analysis in both physical and chemical respects.

Precursor film formation at bitumen/water/air interfaces is clearly seen using ellipsometric thickness measurements of the spreading front. Three different regions are particularly evident when the substrate is deionized water. In the first two regions, relatively uniform surface films are formed, as indicated by the steady ellipsometric data for a deionized water subphase in Fig. 5(a). It is seen that the presence of rapid-spreading constituents initially produces a film of

thickness ~ 30 -50 nm after approximately 15-30 s. It is not unreasonable to consider that the initial film would contain the most surface-active species possessing the highest (positive) spreading coefficients. Less surface-active components would be expected to contribute to the thicker films in the range 150-180 nm that are seen to form more slowly. We have shown that these parallel the film pressure measurements which, for deionized water, reach ~ 12 -14 mN/m at the maximum film thickness (Fig. 6(a)). However, in the third region, following the attainment of a maximum thickness, it can be seen that the film thickness becomes increasingly irregular, suggesting that the film becomes more dilute and patchy as the supply of further surface-active components becomes exhausted.

By including ~ 0.5 mol/L sodium chloride or calcium chloride in the aqueous subphase, it has also been shown that salinity plays a role in the film development. Although the thickness profiles follow the same general trends for all the subphases, there are some subtle differences. The first region is seen to be less distinct in the presence of the salts, although it can be inferred that the film thicknesses are similar for the three systems. The maximum film thicknesses are also very similar. In the final region, the erratic behavior for the saline solutions appears to be more pronounced than for deionized water. Generally, however, under the same neutral pH conditions for all the subphases, it is evident that the film pressure measurements follow the ellipsometric profiles reasonably well.

The initial thickness of ~ 30 nm for the most rapidly spreading film is around an order of magnitude thicker than a typical surfactant monolayer. It might reasonably be expected, therefore, that the “molecular layer” structure depicted in Fig. 1 contains a complex mixture of surface-active bitumen components and could therefore be considerably thicker than a traditional monolayer. Bearing this in mind, and based on the present findings, another picture emerges with regard to the mechanism of precursor film formation. It has been established that

a bitumen drop will not spread in the absence of surface-active components; the spreading coefficient (eq. 1) will be small, of the order of the value for toluene given in Table 3. Additionally, the high viscosity confers resistance to bulk oil flow.

However, as studied theoretically and summarized by Karapetsas et al., the presence of surface-active species in fluid oil phases has been shown to produce some interesting and unexpected features [47]. These workers showed that surfactant-laden oil lenses on aqueous surfaces variously exhibit complete spreading, spreading with retraction, and “beating” phenomena [47]. Thus, notwithstanding that whole crude oil or bitumen present a more complex situation than the model oil/water/surfactant systems considered in the previous work [47], lessons from the model studies may be extremely valuable in developing the earlier scheme (Fig. 1) for precursor film formation, as well as attaching additional significance to this phenomenon.

Thus, upon contacting a water surface, surface-active molecules in the bitumen will begin to adsorb at the bitumen/water interface, as depicted in Fig. 14(a). As this process continues, so the water/oil interfacial tension, γ_{wo} , will decrease and a point will be reached, shown in Fig 14(b), where the interface becomes saturated and based on observations made by Stocker and Bush [48], the resulting low interfacial tension caused by surfactant adsorption causes oscillations at the edge of the lens which induce emulsification of surfactant-rich droplets (Fig. 14(b)). The spreading coefficient (eq. 1) of the ejected droplets is likely to be sufficiently positive (i.e., above a critical spreading coefficient, S_{crit}) for spontaneous spreading and coalescence to occur at the air/water surface. This is the situation shown in Fig. 14(c). Therefore, since bulk bitumen flow will be constrained by its high viscosity, the surface-active components making up the bitumen/water interfacial layer are probably responsible for the precursor film observed in Fig. 3 at the air/water surface. As the supply of surface-active components from the bitumen/water interface is depleted, the film spreading rate will decrease.

Figure 14. Proposed representation of a bitumen (oil) lens at an air/water surface: (a) short time after initial bitumen contact with water surface; (b) just prior to spreading; and (c) just after spreading following expulsion of the precursor film.

This model also suggests that the interfacial material accumulating at bitumen/water interfaces in water-in bitumen emulsions, at least in the early stages, should have a similar composition to the precursor films. Unlike research on precursor films, more extensive research has been conducted using interfacial material derived from an aqueous interface; some of these have involved Athabasca bitumen. For example, Jarvis et al. [49] separated interfacial material by adsorption at a hydrated silica surface from the diluted bitumen enabling the characterization of interfacially-active components using Fourier transform ion cyclotron resonance mass spectrometry. Using a more rigorous analysis than we have adopted for the present study, these workers observed very similar heteroatom class speciation, enabling their conclusion that the interfacial material obtained from Athabasca bitumen contains a higher abundance of acidic oxygen-, nitrogen-, and sulfur-containing species compared to the parent bitumen. The ubiquitous presence of carboxylic acids found in the present study is also consistent with results

obtained elsewhere [50-52]. Using the same bitumen sample, we also extracted material directly from a toluene-diluted bitumen/water interface, from which we identified similar species distributions to those shown in Fig. 10 [53]. However, some differences were apparent: for example, O2 species were more abundant in the precursor film than in the interfacial material, whereas the latter contained species richer in oxygen, including O5, O6, N1O4, N1O5, O5S1, O4S2 and O5S2.

The precursor films generate a modest film pressure of ~ 14 mN/m under the neutral pH conditions of our experiments, and are largely independent of the aqueous subphase. This is consistent with the results given by Drelich et al. for the same pH range [11].

The reduction in surface tension as the precursor film spreads on the water surface is consistent with the chemical composition of the film and the data obtained by other workers [9-11,17]. As supported by the basic compositional analysis from the present study, acid groups (including sulfur acids) identified in the film would be expected to contribute to the film tension. The significance of precursor film spreading in oil recovery (based on three-phase water/oil/solid systems) is related to the effect of precursor film formation and spreading on mineral surfaces which may alter wettability. This would be particularly important for fluid displacement in porous media [54].

Effects on wettability have been seen in the present work in the trends seen on advancing and receding contact angles for successively withdrawn precursor films. We have shown that the film can be easily transferred to an originally hydrophilic solid substrate, which leads to an increase in the water contact angle. Understandably, for a finite amount of film material, the effect decreases with each successive film transfer. The first film transferred receives most hydrophobic film components ($\theta_a \sim 90^\circ$), with the subsequent second and third transfers being

less efficient, manifest in lower θ_a values of $\sim 55^\circ$, together with reduced film adhesion to the glass surface (resulting in lower θ_r values).

The complex composition and diversity of the crude oil components present in the precursor film is evident from the summary given in Fig. 10. It is likely that the principal spreading components are more evident through enrichment in the film. On the other hand, the classes present in the film that are depleted with respect to their relative contribution in the original bitumen are likely to have been carried into the film adventitiously, possibly via Marangoni flow resulting from surface (film) tension gradients. This suggests that the principal spreading components involve the oxygenated classes O1S1, O2, O3, O3S1, O4 and O4S1. Owing to the slight solubility in water of neutral carboxylic acids [55], the presence of the O2 class in the precursor film may be expected, which also agrees with the infrared spectroscopy and SIMS results.

Although not specifically relating to precursor films of the type described herein, there are precedents for similar heteroatom classes identified in various crude oil systems. For example, Qian and Robbins reported the presence of a range of classes, including O2, O3, O4, and O2S1, O3S1 and O4S1, in a South American heavy crude oil [46]. Wang et al. [24] separated a vacuum topped Canadian oil sands bitumen into maltenes and asphaltenes fractions and found similar relative abundances of O2 species in all fractions-, but the asphaltene fractions were enriched in O2S1, O2S2, N1O2 and some higher oxygenated classes. Stanford et al. [23] and Muller et al. [51] reported similar abundances of O2 class species in interfacial materials isolated from water-in-crude oil emulsions as found in the respective original oils, for several geographically distinct conventional and heavy crude oils. However, the analysis also established that the emulsion interfacial materials were enriched in O4S1 species with relative abundances dependent on the crude oil type. These species were proposed to represent, for

example, hydroxylated alkylbenzene sulfonates and hydroxylated alkylsulfonates, which are expected to possess surfactant-like properties.

We consider that the present results could have both general and specific potential implications in the interfacial chemistry of crude oil. There is considerable current interest in mechanisms of crude oil recovery and in particular the way in which water chemistry which governs oil/rock interactions. Knowledge of the composition of interfacial films, which to a large extent dictate the wettability of reservoir mineral surfaces [56], will provide improved understanding of oil recovery mechanisms and could potentially aid the design of new recovery approaches, including new chemical methods. From the results obtained herein, it is apparent that acid species are particularly prominent in the precursor film. This finding is potentially significant in that such chemistry has been implicated in wettability alteration in previous work, including reservoirs [57,58] and production pipelines [56]. The specific finding that fatty (naphthenic) acids are present in the most rapidly spreading film, for example, is consistent with results of Gomari and Hamouda who found that oil-soluble fatty acids are significant in increasing the oil-wet nature of calcite surfaces [58].

On the basis of our findings in support of Drelich's previous work [9-11], we have shown that mixing bitumen and water at an air surface leads to segregation of surface-active species, which influence the wettability of a subsequently introduced solid surface. The role of the interfacial films thus produced could have general significance for the wettability of crude oil/brine/rock systems as found in all crude oil reservoirs. For example, it has been reported that residual organic species present on the surface of toluene-extracted oil sands solids contain different molecular species than the expected asphaltic components, including sulfoxides, sulfones and nitrogen heterocycles [59], as identified above, the presence of which may therefore possibly be a consequence of films spread by mechanisms discussed in the present paper.

5. Conclusions

The present study set out to report on the physical and chemical properties of so-called precursor films [9-11,17] formed by spreading of selective components from a sample of an Athabasca oil sands bitumen. Unlike a pure oil drop at a water surface, which can either spread or remain at equilibrium as a lens depending on system thermodynamics, kinetic factors primarily dictate the behavior of crude oils. Precursor film spreading is only evident at the bitumen/water/air three-phase contact point, with no partitioning of surface-active components between bitumen and water being observed in the absence of an air interface. Film spreading characteristics have been monitored on aqueous solutions using ellipsometry and film pressure measurements, the former providing an estimate of the maximum thickness of the spreading films of ~150-180 nm, a value that has not been measured hitherto. Corresponding film pressure measurements are in agreement with previous studies [11].

Contact angle measurements made on precursor films transferred to glass slides show the film material to be hydrophobic, suggesting a possible mechanism for their involvement in wettability modification in crude oil reservoirs [60].

Infrared spectroscopy and mass spectrometry have identified aspects of the chemical composition of precursor films for the first time. The infrared spectra have revealed the film to be enriched in $>C=O$, $>C=C<$ (aromatic), and $>S=O$ functionalities, possibly including $-O-H$ (or $>N-H$) groups. These general features agree with several of the species classes observed in the precursor films using SIMS and HRMS techniques. The SIMS spectra, for example, reveal the presence of carboxylic (naphthenic) acids and aromatic fragments. The HRMS analysis, on the other hand, is more useful for identifying hetero-species classes. From the negative ESI spectra, for example, in addition to the O2 class (which includes carboxylic acids), O3 and O4 class species are also prominent, together with various sulfur/oxygen classes that have also

been identified by other workers in a range of other crude oils and fractions. On the basis of structures suggested from HRMS species abundance plots for the different identified heteroatom classes [23], many will be expected to be interfacially-active. With the foregoing in mind, it is entirely possible that selectivity in spreading components can lead to wettability modification, with naturally water-wet surfaces becoming more hydrophobic.

ACKNOWLEDGEMENTS

Initial contributions from BP America are gratefully acknowledged, in particular, for establishing the CPSC at the University of Surrey and for the provision of a studentship to VG. Thanks are due to Drs. Chrissie Wicking and Huang Zeng of BP for HRMS analysis and valuable discussions, and Dr. Steve Hinder and Ms. Judy Peters of the University of Surrey for SIMS and elemental analysis, respectively.

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