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Interfacial Tension of Bitumen–Water Interfaces. Part 1: Influence of Endogenous Surfactants at Acidic pH[†]

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We have studied the time dependence of the interfacial tension between acidic aqueous solutions (pH 2) and commercial straight-run bitumen droplets of different origins by the pendent drop method. Because of the existence in bitumen of naturally occurring surface-active species, significant changes of the interfacial tension are observed over timescales of several thousands of seconds. The kinetics of the decrease is consistent with the exodiffusion of endogenous surfactants toward the bitumen–water interface and throughout the bitumen matrix. At $T = 90\text{ }^{\circ}\text{C}$, one observes that the interfacial tension decreases as $t^{1/2}$ at short times and as $t^{-1/2}$ at long times when the interface becomes nearly saturated. Combining these two kinetic data allows for a direct estimate of the surface concentration of these endogenous surfactants. If one makes the assumption that they organize in a dense, close-packed monolayer, their size and concentration in bulk bitumen can also be readily derived. At $T = 140\text{ }^{\circ}\text{C}$, the viscosity of bitumen is 20 times lower than at $90\text{ }^{\circ}\text{C}$ and the short time kinetics can no longer be resolved with our experimental apparatus. This restricts the data analysis, but we can nevertheless obtain an estimate of the size of the surfactant molecules if one makes the reasonable hypothesis that the bulk concentration of surfactants remains unchanged between 90 and $140\text{ }^{\circ}\text{C}$. Our results suggest that the surface-active species at pH 2 are asphaltene moieties of basic character. They are probably in an aggregated form because the measured, nanometric size decreases at elevated temperatures. Quite remarkably, they correspond to a very small fraction of the total asphaltenes contained in bitumen, which explains why they are extremely difficult to detect analytically. To the best of our knowledge, this is the first time that quantitative data on the endogenous surfactants are obtained in industrial bitumen. The present results thus complete the numerous existing observations on model oil–water systems.

1. Introduction

Bitumen emulsions are encountered more and more frequently in industrial applications, especially in road technology for surface repair and cold mix constructions.¹ Indeed, the fact that they are fluid at room temperature makes them easier to handle than bulk bitumen that is highly viscous, especially at low temperatures. These water-based bitumen emulsions are formed by online mixing of water, bitumen, and small amounts of surface-active additives, in a powerful turbine and at high temperatures.^{2,3} The role of these additives is to facilitate the dispersion process by adsorbing at the oil–water interface.^{4–6}

Because they lower the interfacial tension, they allow for a reduction of the mean size of the bitumen droplets for a given mechanical energy and duration of mixing. Typical sizes are in the range of a few tens of micrometers. They also contribute to the stability of the emulsion during storage by decreasing the rate of droplet coalescence upon collision.

The commercial additives generally used by industry are low-molecular-weight fatty amines or fatty acids in the case of ionic emulsions and fatty epoxies in the case of nonionic ones. They are dissolved in water at low concentrations, typically between 0.01 and 1% by weight, and this is amply sufficient to cover the bitumen–water interface with a dense monolayer of surface-active molecules.

It has been increasingly realized, however, that some of the molecules present in bitumen are naturally surface-active.^{7–10} In this paper, we investigate the interfacial properties of seven straight-run bitumen of different origins and compositions. We monitor the interfacial tension of bitumen droplets in contact with an aqueous acidic solution by the pendent drop method. The measurements are performed over an extensive time period,

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Table 1. Physical and Chemical Characteristics of the Tested Bitumen^a

bitumen type	A	B	C	D	E	F	G
acid index (mg of KOH/g)	2.3	0.2	0.1	4.0	<0.1	1.9	2.3
asphaltene content (%)	11.1	9.6			8.7	10.1	13.0
density at 25 °C (g/cm ³)	1.022	1.023	1.025	1.017	1.022	1.023	1.022
density at 90 °C (g/cm ³)	0.984	0.983	0.984	0.979	0.984	0.982	0.983
density at 140 °C (g/cm ³)	0.954	0.953	0.953	0.950	0.954	0.951	0.953

^a The seven different bitumen are labeled “A–G”.

and we fit the data with simple diffusion laws that allow us to extract the main characteristic of the endogenous surfactants active at pH 2: molecular size and bulk and surface concentrations. We also attempt to specify their chemical nature. Such quantitative characterization could be advantageously used for emulsion production. In particular, we will compare their capacity to lower the bitumen–water interfacial tension with those of commercially available products.

2. Materials

2.1. Bitumen Samples. A series of 180/220-grade bitumen was selected from six Western European refineries. They represent a good panel of the bitumen available on the market and, in particular, cover a wide range of acid indices. Their physicochemical characteristics are listed in Table 1. Their viscosities have not been indicated explicitly, but they are all very similar, typically 2.8 Pa s at 90 °C and 0.16 Pa s at 140 °C.

Their acid indices were measured by dissolving 2 g of each bitumen in 150 mL of toluene and adding 75 mL of isopropanol and 1 mL of water to this solution. The acidic groups of the bitumen were then titrated with 0.2 mg aliquots of alcoholic potassium hydroxide (0.1 N KOH). Bitumen B, C, and E have low acid indices, typically below 0.2 mg of KOH/g. Bitumen A, D, F, and G are more acidic, with acid indices between 1.9 and 4.0 mg of KOH/g. Bitumen G has been obtained from bitumen F by adding 0.3% by weight of abietic acid, a naphtheno-aromatic compound bearing one carboxylic acid group.

The bitumen density was measured at 25 °C with a picnometer, according to the NF normalized procedure number 60 007, and at 140 °C, with an oscillating capillary densitometer, according to the NF procedure number 60 172. The density at 90 °C has been estimated by linearly interpolating the values at 25 and 140 °C. The measuring accuracies were $\pm 1 \times 10^{-3}$ g cm⁻³ in the first case and $\pm 2 \times 10^{-3}$ g cm⁻³ in the second case.

The asphaltene content (by weight) of five of the seven bitumen was measured by the method of precipitation in heptane.^{3,11} The measurement accuracy was $\pm 1.5\%$.

2.2. Commercial Surfactants. The “exogenous” surfactants used in this study, Emulsamin L60, Stabiram MS3, and Polyram SL were obtained commercially from CECA (Cours Michelet, 92091 Paris-La Défense, France). They were used as received, without further purification. Emulsamin L60 is a mixture of alkylamido polyamines obtained by saponification of tallow triglycerides. They possess two polar groups and have a molecular weight of approximately 450 Da. Stabiram MS3 is a biquaternary ammonium salt with a single 18 carbon hydrocarbon chain. Its molecular weight is 474. Polyram SL is a linear molecule composed of a tallow fatty chain of 16–18 carbon atoms connected to four propylene diamine groups. Its molecular weight is 538 Da. Aqueous solutions of these surfactants (concentrations between 0.01 and 0.1 g/L) were acidified at pH 2 by the addition of hydrochloric acid. In this process, the amines are neutralized and form chlorohydrates that are more water-soluble. Amine chlorohydrates were thus the effective emulsifying species. The protonated form of Emulsamin

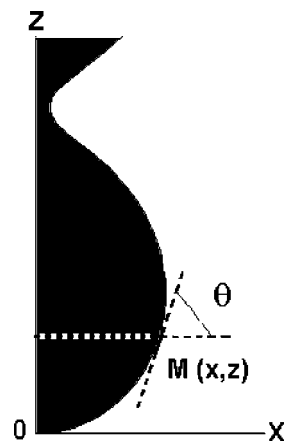


Figure 1. Typical profile of the hanging drop method (assuming cylindrical symmetry around the vertical axis).

L60, Stabiram MS3, and Polyram SL bear two, two, and four positive charges, respectively.

3. Experimental Methods

3.1. Interfacial Tension Measurements by the Hanging Drop Method. A bitumen droplet of known volume is formed at the tip of a hypodermic needle immersed in an aqueous solution. The pendent drop is axisymmetric if the arrangement is vertical, and the balance between the interfacial tension and the buoyancy forces controls its shape. The interfacial tension tends to make the drop spherical, whereas the gravity tends to elongate it. At any point M on the bitumen–water interface (Figure 1), the two principal radii of curvature, R and R' , obey the Laplace equation

$$\Delta P = \gamma \left(\frac{1}{R} + \frac{1}{R'} \right) \quad (1)$$

where ΔP is the pressure difference between the inner and outer media and γ is the interfacial tension.

Across the horizontal plane passing by M , the equilibrium of the forces yields a second equation relating ΔP to the volume, V , of the drop beneath the plane

$$2\pi x \gamma \sin \theta = V \Delta \rho g z + \pi x^2 \Delta P \quad (2)$$

where x and z are the coordinates of M ($z = 0$ corresponds to the apex of the drop), θ is the polar angle of the tangent to the drop at the M position, $\Delta \rho$ is the specific gravity difference between bitumen and water, and g is the gravitational constant.

The most obvious way to obtain the interfacial tension, γ , is to combine eqs 1 and 2. However, this method can be tedious because it requires solving a set of differential equations. An easier method is to perform a drop shape analysis at an arbitrary array of coordinate points selected along the drop profile and make a least-squares fit between the theoretical and experimental drop profiles.¹² Cheng et al.¹³ and Labourdenne et al.¹⁴ have further refined this approach. The accuracy on the determination of γ critically depends upon the value of the bond number, $B = \Delta \rho g R_a^2 / \gamma$, where R_a is the radius of curvature at the apex of the droplet. If B is small, the gravity forces are almost negligible compared to the capillary forces and the uncertainty is very large. On the contrary, if B is close to unity, the uncertainty is significantly reduced. For instance, the error on γ is 12% if $B = 0.01$ but only 0.3% if $B = 0.4$. For a given experimental system, the value of B can be adjusted via the drop volume V . Indeed, the radius of curvature, R_a , at the apex scales as $V^{-1/3}$

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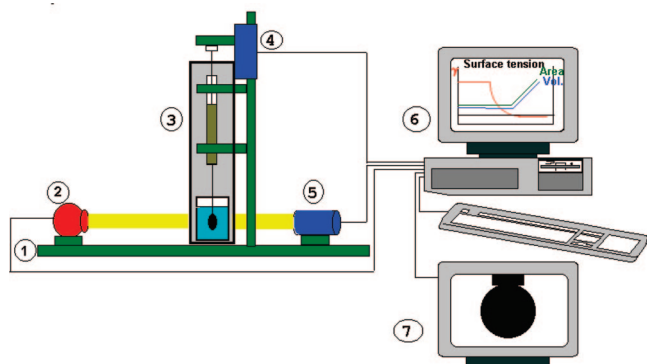


Figure 2. Schematic setup of the oil drop tensiometer optical table (1), light source (10 W halogen lamp, Osram) (2), pressure chamber containing the 25 mL cuvette with the aqueous solution and the hypodermic needle (3), computer-controlled dc motor drive for the syringe piston (4), CCD camera (JAI CV-M50, Japan) (5), Microcomputer Pentium III 550 MHz (Dell, Round Rock, TX) (6), and video monitor (Philips) (7).

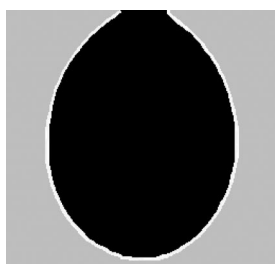


Figure 3. Image of a 300 μL hanging droplet of bitumen in the pressure chamber at 140 $^{\circ}\text{C}$. The droplet is in contact with an aqueous solution at pH 2. The solid line is the best fit to the Laplace equation (see eqs 1 and 2 in the text).

to a good approximation. The uncertainty on $\Delta\rho$ also plays a role, and knowledge of the specific gravity to the fourth digit is generally desirable to keep the relative error on this parameter below 0.1%.

3.2. Experimental Setup. The volume of the bitumen drop was between 10 and 300 μL , whereas the volume of the aqueous solution was much larger, on the order of 25 mL. The setup (Figure 2) was temperature-controlled between 20 and 200 $^{\circ}\text{C}$, with an accuracy of 0.5 $^{\circ}\text{C}$. A long-term stability of ± 0.5 $^{\circ}\text{C}$ was achieved using a platinum resistance in the feedback loop. For temperatures above 100 $^{\circ}\text{C}$, it was necessary to pressurize the cell to 10 bar with an inert gas (nitrogen) to avoid boiling. The drop was illuminated by a diffuse light source (10 W halogen lamp, Osram), and its projected profile was analyzed by a CCD camera (JAI CV-M50, Japan) connected to a dedicated computer equipped with fast image analysis (25 frames per second) software. The pixel size was 5 μm , and a subpixel algorithm was used to numerically increase the lateral resolution to 1 μm . The optical measurements were started as soon as the drop had reached mechanical equilibrium, a process that could take between 1 and 20 s depending upon bitumen viscosity. Snapshots were taken every tenth of a second at the start of the experiment when the drop shape variations are most rapid and every second at longer times when the drop approaches equilibrium. The evolution of the drop shape was monitored up to 6000 s.

3.3. Determination of the Interfacial Tension. A typical profile is shown in Figure 3 for a 300 μL bitumen droplet at 140 $^{\circ}\text{C}$. The radius of curvature at the apex is 410 μm , and the bond number is 0.13, taking a $\Delta\rho$ value of 20 kg m^{-3} . The thick solid line surrounding the drop corresponds to the least-squares fit to the experimental profile, using eqs 1 and 2. The maximum deviation

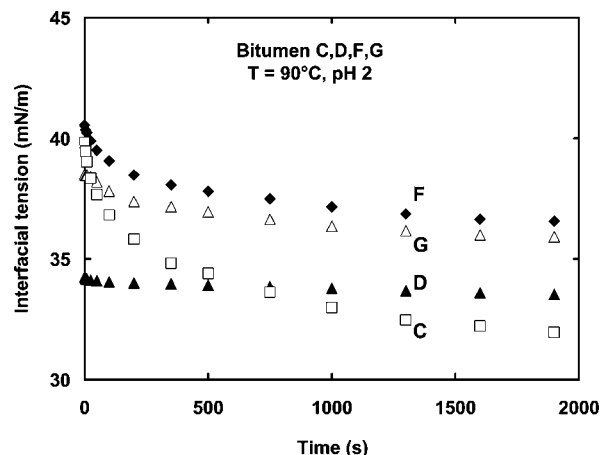


Figure 4. Time evolution of the interfacial tension, γ , between bitumen and acidified water (pH 2). Data are for bitumen "C", "D", "F", and "G". $T = 90$ $^{\circ}\text{C}$.

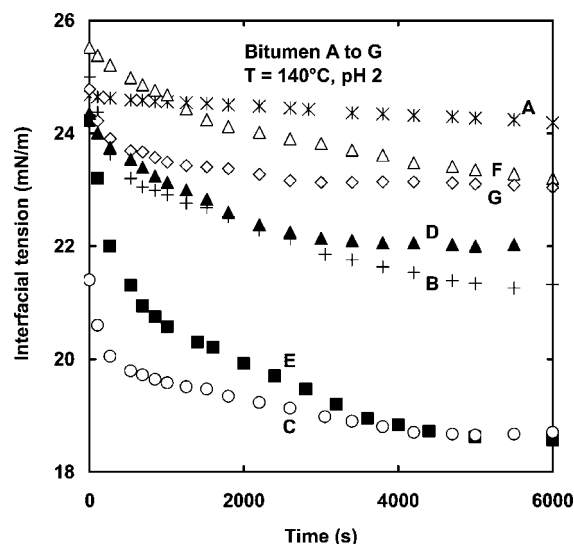


Figure 5. Time evolution of the interfacial tension, γ , between bitumen and acidified water (pH 2). Data are for seven bitumen of different origin, labeled "A–G". $T = 140$ $^{\circ}\text{C}$.

at any point along the droplet is less than 5 μm , and the fit yields an interfacial tension value of 25 mN m^{-1} , to an accuracy of ± 0.5 mN m^{-1} .

4. Results

The interfacial tension between bitumen and water has been measured as a function of time for two different temperatures, 90 and 140 $^{\circ}\text{C}$, and at a pH of 2. This acidic value is commonly used in the fabrication of cationic bitumen emulsions. Similarly, 90 $^{\circ}\text{C}$ is the most preferred temperature in industrial emulsification, and 140 $^{\circ}\text{C}$ is the temperature at which bitumen is initially brought in contact with water. Measurements with aqueous solutions containing known concentrations of commercial surfactants have also been performed for a comparison.

4.1. Time Dependence of the Interfacial Tension at Fixed Temperature. The results obtained for several bitumen are shown in Figure 4 ($T = 90$ $^{\circ}\text{C}$) and Figure 5 ($T = 140$ $^{\circ}\text{C}$). In all cases, the interfacial tension decreases with time and finally reaches a plateau value. Most curves display a rapid drop during the first 600 s, followed by a slower evolution at longer times. Even at the higher temperature of 140 $^{\circ}\text{C}$, the variations are still significant up to 6000 s. The range of the decrease strongly depends upon the type of bitumen. All kinds of

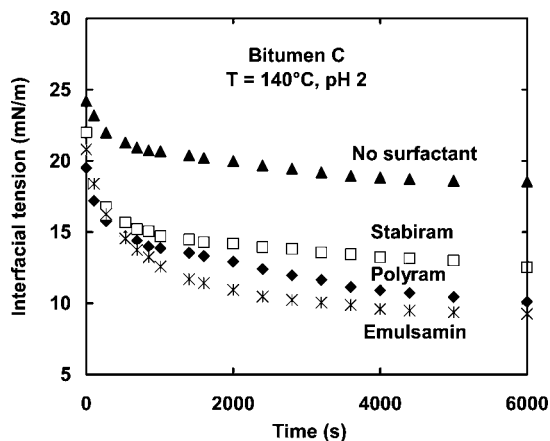


Figure 6. Time evolution of the interfacial tension, γ , between bitumen “C” and acidified (pH 2) aqueous solutions containing known amounts of commercial surfactants: Emulsamin, Polyram, and Stabiram at concentrations of 0.1, 0.1, and 0.033 g/L, respectively. The curve in the absence of commercial surfactants is shown for a comparison. $T = 140\text{ }^{\circ}\text{C}$.

variations are observed, from large ones to very small ones. For instance, the interfacial tension change is 8 mN m^{-1} for bitumen C at $90\text{ }^{\circ}\text{C}$ and almost absent for bitumen D. A second important feature is that the ranking order found at $90\text{ }^{\circ}\text{C}$ is preserved at $140\text{ }^{\circ}\text{C}$. For instance, bitumen C (F) has the lowest (highest) interfacial tension at long times among all tested samples at both 90 and $140\text{ }^{\circ}\text{C}$. These results are good evidence for the presence of natural (“endogenous”) surfactants in bitumen that are able to migrate to the bitumen–water interface. Moreover, the amplitude of the interfacial tension decrease is clearly connected to the composition of bitumen.

The interfacial tensions for droplets of bitumen C at $140\text{ }^{\circ}\text{C}$ in contact with aqueous solutions containing known concentrations of commercial surfactants have also been measured. Figure 6 shows the results for bitumen C in contact with solutions of Emulsamin, Polyram, and Stabiram at concentrations of 0.1, 0.1, and 0.033 g/L, respectively. The time dependences are qualitatively similar to those observed for endogenous surfactants (see the corresponding curve plotted on the same graph). The range of the interfacial tension decrease, however, is somewhat larger. It varies between 11 and 15 mN m^{-1} for the three surfactants tested, whereas it was 5 mN m^{-1} previously. This difference can stem from two separate effects, a lower concentration of the potentially active surfactants on the one hand or a lower efficiency at the particular pH on the other hand. Obviously, the natural surfactants present in bitumen are not as efficient as the commercial ones for the bitumen–water interface.

4.2. Influence of Thermal Cycling on the Final Interfacial Tension Value. In this set of experiments, the temperature of the sample has been changed during the time course of the experiment. First, the interface between the bitumen and the acidified water is allowed to equilibrate at a specific initial temperature. Then, the temperature is ramped to a final value, either lower or higher, at a rate of $0.5\text{--}1.5\text{ }^{\circ}\text{C min}^{-1}$.

Figure 7 shows the variation of the interfacial tension for bitumen C as the temperature is decreased from 140 to $90\text{ }^{\circ}\text{C}$, after a waiting time of 30 min at $140\text{ }^{\circ}\text{C}$. The final temperature of $90\text{ }^{\circ}\text{C}$ is then maintained until the interfacial tension reaches a plateau value. During this process that lasts for approximately 1800 s , the interfacial tension changes from 21 to 27 mN m^{-1} . This final value is markedly lower than the value obtained when the temperature of the interface has been maintained at $90\text{ }^{\circ}\text{C}$ at all times. Inserting the data of Figure 4 on the same graph

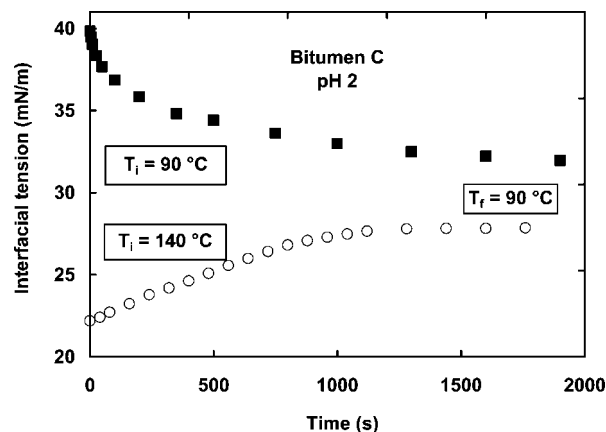


Figure 7. Time evolution of the interfacial tension, γ , between bitumen “C” and acidified water (pH 2). (Top curve) Temperature is maintained at $90\text{ }^{\circ}\text{C}$. (Bottom curve) Temperature is decreased from 140 to $90\text{ }^{\circ}\text{C}$ at a sweep rate of $0.5\text{ }^{\circ}\text{C min}^{-1}$.

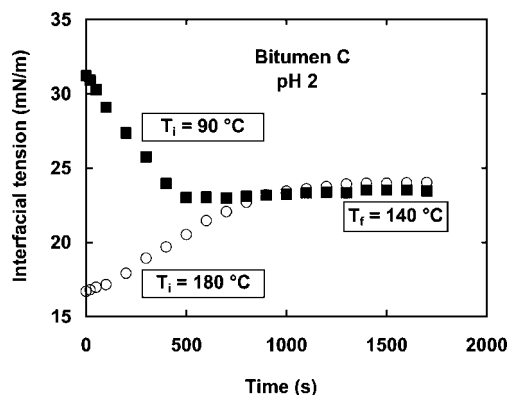


Figure 8. Time evolution of the interfacial tension, γ , between bitumen “C” and acidified water (pH 2). (Top curve) Temperature is increased from 90 to $140\text{ }^{\circ}\text{C}$. (Bottom curve) Temperature is decreased from 180 to $140\text{ }^{\circ}\text{C}$. Sweep rate is $0.5\text{ }^{\circ}\text{C min}^{-1}$ in both cases.

reveals a difference of 5 mN m^{-1} . This behavior is quite general, and even higher discrepancies have been observed for some bitumen, for instance, 14 mN m^{-1} in the case of bitumen F (data not shown). The fact that the plateau value on the sample maintained at $90\text{ }^{\circ}\text{C}$ is systematically higher suggests that the 30 min duration of the experiment is not sufficient for the endogenous surfactant molecules to exodiffuse toward the bitumen–water interface and form a dense overlayer. Viscosity of bitumen at $90\text{ }^{\circ}\text{C}$ is 20 times larger than at $140\text{ }^{\circ}\text{C}$. Therefore, maintaining the sample at this temperature for 1800 s is equivalent to a process time of 90 s only at $140\text{ }^{\circ}\text{C}$. It is thus very logical that the true equilibrium has not yet been reached.

Figure 8 shows similar experiments but with a final temperature of $140\text{ }^{\circ}\text{C}$. For the bottom curve, the sample has been equilibrated at $180\text{ }^{\circ}\text{C}$ and then ramped down to $140\text{ }^{\circ}\text{C}$. For the top curve, the initial temperature was $90\text{ }^{\circ}\text{C}$ and was then ramped up to $140\text{ }^{\circ}\text{C}$. Strikingly, the interfacial tension values at long times are identical in both experiments. This implies that, during the course of the experiment, the sample had enough time to reach true equilibrium; the final interfacial state is now independent of the sample thermal history.

5. Data Analysis

The present experiments show that the interfacial tension for bitumen droplets in contact with water is time-dependent, even if the aqueous solution contains no surfactant molecules. This behavior that has also been observed by others (see for example

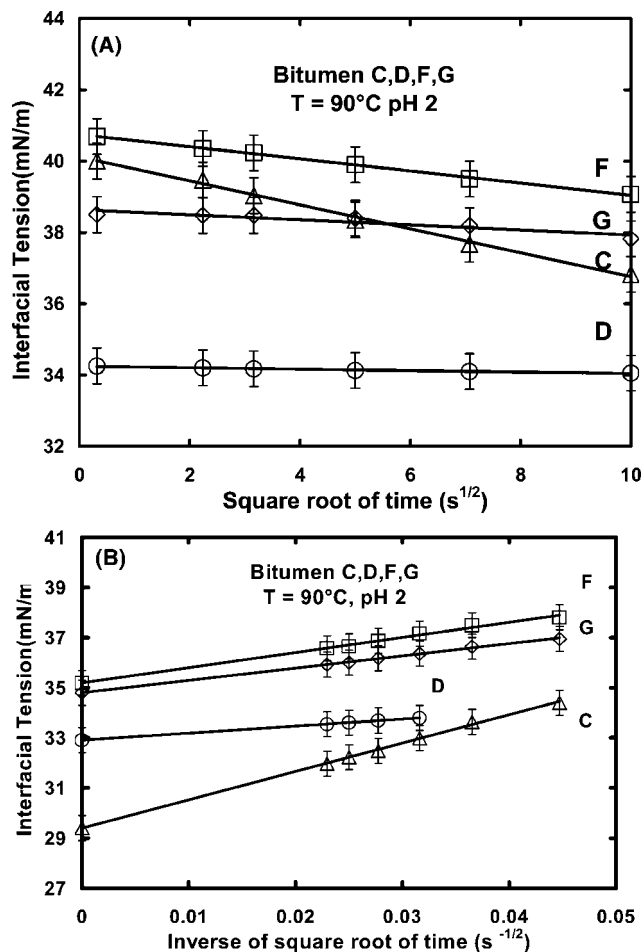


Figure 9. Time evolution of the interfacial tension, γ , between four different bitumen, labeled “C”, “D”, “F”, and “G”, and acidified water (pH 2). $T = 90^\circ\text{C}$. (A) Interfacial tension is plotted versus the square root of time. The time window is 0–100 s. The solid lines are the best fits to a straight line, as expected in the short-time regime. (B) Interfacial tension is plotted versus the inverse square root of time. The time window is 500–2500 s. The solid lines are the best fits to a straight line, as expected in the long-time regime.

the reference by Li et al.¹⁵ provides a clear indication that the bitumen matrix contains intrinsic, endogenous, surface-active molecular components that can migrate to the bitumen–water interface. Their progressive accumulation induces the change in the interfacial tension. The decreases are significant and range between 2 and 7 mN m^{-1} , depending upon the nature of the bitumen. They are however smaller than the 13 mN m^{-1} value typically observed when deliberately adding exogenous polyamine surfactants to the aqueous side.

5.1. Quantitative Analysis of the Time Dependence of the Interfacial Tension. The variation of the interfacial tension, $\gamma(t)$, is controlled by the diffusion of the endogenous surfactants within the bitumen matrix, in the same way as exogenous surfactants can move by Brownian motion in the aqueous solution. The accumulation of surface-active materials at interfaces is called the surface excess, $\Gamma(t)$. For diffusion-limited processes, it is described by the Ward and Tordai equation¹⁶

$$\Gamma(t) = 2C_b\sqrt{D_T t/\pi} - 2\sqrt{\frac{D_T}{\pi}} \int_0^{\sqrt{t}} C_s d(\sqrt{t} - \tau) \quad (3)$$

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The parameters D_T , C_b , and C_s are the translational diffusion coefficient, bulk concentration, and subsurface concentration, respectively. τ is a dummy variable of integration.

Fainerman et al.¹⁷ have given asymptotic solutions for $\Gamma(t)$ in the limit of short time (ST) and long time (LT). They have also proposed simple expressions for the time dependence of the interfacial tension decrease, $\Delta\gamma(t)$, by relating the surface excess to the interfacial pressure. At short times, one uses the Henry adsorption isotherm, and at long times, one uses the Gibbs equation. The interfacial tension decreases in the two regimes are

$$\Delta\gamma(t)_{\text{ST}} = \gamma_0 - \gamma(t) = -2RTC_b\sqrt{D_T t/\pi} \quad (4)$$

and

$$\Delta\gamma(t)_{\text{LT}} = \gamma(t) - \gamma_\infty = -RT(\Gamma_{\text{sat}})^2\sqrt{\frac{\pi}{4D_T t}}C_b^{-1} \quad (5)$$

where R is the gas constant and Γ_{sat} is the surface excess at saturation.

At short times, the interface is still dilute and $\Delta\gamma(t)_{\text{ST}}$ is proportional to C_b and the square root of time. At long times, the saturation of the interface restricts the accessibility and $\Delta\gamma(t)_{\text{LT}}$ varies inversely proportional to C_b and the inverse of the square root of time. It is to be noted that the same diffusion coefficient D_T value is applicable at short and long times because the diffusion in bulk bitumen is not affected by the saturation of the interface.¹⁸

These asymptotic variations can be used to access quantitative information on the diffusing species, namely, their bulk concentration C_b , their radius r , and their surface excess at saturation Γ_{sat} . The surface excess can be obtained directly from the arithmetic product of the slopes of $\Delta\gamma(t)_{\text{ST}}$ versus $t^{1/2}$ and $\Delta\gamma(t)_{\text{LT}}$ versus $(t')^{-1/2}$. Indeed, one has

$$\text{slope of } \Delta\gamma(t)_{\text{LT}} \times \text{slope of } \Delta\gamma(t')_{\text{ST}} = (RT\Gamma_{\text{sat}})^2 \quad (6)$$

With only two equations, it is not possible to extract the other parameters, r and C_b independently. However, if one considers that the bitumen–water interface is totally covered by the endogenous surfactants at long times, one can write a simple relationship between Γ_{sat} and D_T . Indeed, for close-packed molecules, the molecular cross-section $A = \pi r^2$ is related to Γ_{sat} by $A = (N\Gamma_{\text{sat}})^{-1}$, where N is Avogadro’s number. Therefore, one has

$$r = (\pi N\Gamma_{\text{sat}})^{-1/2} \quad (7)$$

Once r is known, the diffusion coefficient D_T can be estimated by using the Stokes–Einstein equation law

$$D_T = kT/6\pi\eta r \quad (8)$$

where η is the bulk viscosity of the bitumen.

Finally, one obtains the bulk concentration C_b from

$$C_b = \text{slope of } \Delta\gamma(t)_{\text{ST}}/(2RT(D_T/\pi)^{1/2}) \quad (9)$$

5.2. Determination of Γ_{sat} , r , and C_b for the Endogenous Surfactants at pH 2 and $T = 90^\circ\text{C}$. The data of Figure 4 have been replotted versus the square root of time and the

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(18) The possibility of a strong barrier to adsorption has not been considered. In that case, the adsorption process becomes kinetically controlled rather than diffusion-controlled and the equations of Ward and Tordai are no longer applicable. Bauguet et al. have briefly described such a situation (see ref 26).

Table 2. Analysis of the Time Behavior of the Interfacial Tension, γ , at $T = 90\text{ }^{\circ}\text{C}$ and pH 2

bitumen	short-time regime		long-time regime		γ_0 (mN/m)	γ_{∞} (mN/m)
	time interval (s)	exponent α	time interval (s)	exponent β		
C	0–100	0.53	500–1900	−0.51	39.9	29.4
D	0–100	0.49	1000–1900	−0.44	34.2	32.2
F	0–100	0.53	500–1900	−0.51	40.7	35.2
G	0–100	0.51	500–1900	−0.50	38.6	34.8
estimated error		± 0.03		± 0.03	± 0.5	± 0.5

Table 3. Characteristic Parameters of the Endogenous Surfactants at $T = 90\text{ }^{\circ}\text{C}$ and pH 2

bitumen	slope of ST (mN/m/s ^{−1/2})	slope of LT (mN/m/s ^{−1/2})	Γ_{sat} [10^{-6} (mol/m ²)]	r (nm)	D_T [10^{-13} (m ² /s)]	C_b [10^{-1} (mol/m ³)]	$\Delta\gamma = \gamma_0 - \gamma_{\infty}$ (mN/m)
C	−0.32	113.4	2.0 ($\pm 20\%$)	0.51 ($\pm 10\%$)	1.8 ($\pm 10\%$)	2.2 ($\pm 35\%$)	10.6
D	−0.06	28.0	0.43 ($\pm 100\%$)	1.1 ($\pm 50\%$)	0.85 ($\pm 50\%$)	0.60 ($\pm 180\%$)	2.0
F	−0.16	59.8	1.0 ($\pm 40\%$)	0.72 ($\pm 20\%$)	1.3 ($\pm 20\%$)	1.3 ($\pm 80\%$)	5.5
G	−0.07	48.5	0.61 ($\pm 80\%$)	0.93 ($\pm 40\%$)	1.0 ($\pm 40\%$)	0.65 ($\pm 180\%$)	3.8
estimated error	± 0.10	± 10					± 1.0

inverse square root of time in parts A and B of Figure 9, respectively. One observes that the variation of the interfacial tension with time can be well-fitted by a straight line, as predicted by eqs 4 and 5.

The short-time regime extends up to 100 s. This result is coherent with experiments by Eastoe et al.,¹⁹ in which the adsorption of surfactants at the free surface of an aqueous solution was monitored versus time. They found a characteristic time of 10 ms. Because the viscosity of bitumen at $90\text{ }^{\circ}\text{C}$ (2.8 N s m^{-1}) is 4 orders of magnitude higher than that of water ($3.2 \times 10^{-4}\text{ N s m}^{-1}$), this translates into a typical value of 100 s for adsorption of surfactants dispersed in bitumen.

The long time behavior is observed after 1000 s and corresponds to the diffusion-limited adsorption of the surface-active species on an already crowded surface.

The intercept with the ordinate axis in the short and long term regimes yields the interfacial tension values at zero and infinite times, γ_0 and γ_{∞} , respectively (see parts A and B of Figure 9). The slopes of the linear curves can then be determined, and their product yields Γ_{sat} according to eq 6. The values for these straight-run bitumen obtained by distillation in refineries range from 1.9×10^{-7} to $2.0 \times 10^{-6}\text{ mol m}^{-2}$. Such values are of the same order of magnitude as the data by Yarranton for Athabasca sand-extracted bitumen (see Table 6 of ref 20). The highest value is obtained for bitumen C, and we will see later that this is logical in view of its asphaltene content. From the Γ_{sat} values, one deduces the size r or, equivalently, the diffusion coefficient D_T as discussed in the above (see eq 7). Finally, using eq 8, we can derive the values of the bulk concentration, C_b . All of the data that characterize the surface-active molecules present in bitumen C, D, F, and G at pH 2 and $90\text{ }^{\circ}\text{C}$ are summarized in Tables 2 and 3. One notices that the size, r , of the diffusing species is nanometric and varies in a narrow region between 0.5 and 1.65 nm. The diffusion coefficients, D_T , range between 1.8×10^{-13} and $5.7 \times 10^{-14}\text{ m}^2\text{ s}^{-1}$. The C_b values are found to be remarkably small. Dependent upon the bitumen type, they range from 2.4×10^{-2} to $1.3 \times 10^{-1}\text{ mol m}^{-3}$. This suggests that the surface-active species are only a minority component of the bitumen. At this point, we cannot yet say if they are saturated aliphatics, aromatics, resins, or asphaltenes. We have checked that this bulk concentration is still amply sufficient to form a dense monolayer of endogenous surfactants at the bitumen–water interface by

Brownian diffusion in the 6000 s time course of the experiment. Using the D_T and r values of Table 3, a straightforward calculation indicates that there is at least a 3-fold excess of endogenous surfactants.

The γ_0 , γ_{∞} , and $\Delta\gamma = \gamma_0 - \gamma_{\infty}$ values are given in the last three columns of Tables 2 and 3. The overall interfacial tension decrease because of the adsorption of endogenous bitumen surfactants varies between 2 and 11 mN m^{−1} depending upon the bitumen type.

5.3. Determination of Γ_{sat} , r , and C_b for the Endogenous Surfactants at pH 2 and $T = 140\text{ }^{\circ}\text{C}$. The analysis at $T = 140\text{ }^{\circ}\text{C}$ cannot be directly copied from the one at $90\text{ }^{\circ}\text{C}$ because we have not been able to detect the short-time regime. Because bitumen viscosity is 20 times smaller (0.16 N s m^{-1}) at $140\text{ }^{\circ}\text{C}$ than at $90\text{ }^{\circ}\text{C}$, all of the diffusion processes are accelerated. The time window during which it is possible to observe the early adsorption regime is reduced from 100 to 5 s. This regime is therefore not observable experimentally because it is completed before the droplet has time to equilibrate mechanically after being forced out from the syringe.

The data analysis for the long-time regime is shown in Figure 10 based on the data of Figure 5. The experimental points align reasonably well on a straight line when γ is plotted versus the inverse of the square root of time. The linear extrapolation at infinite time yields the γ_{∞} value, and the long-time slope (slope of LT) can be estimated. These values are reported in Table 4 for bitumen C, D, F, and G at pH 2 and $140\text{ }^{\circ}\text{C}$. The other

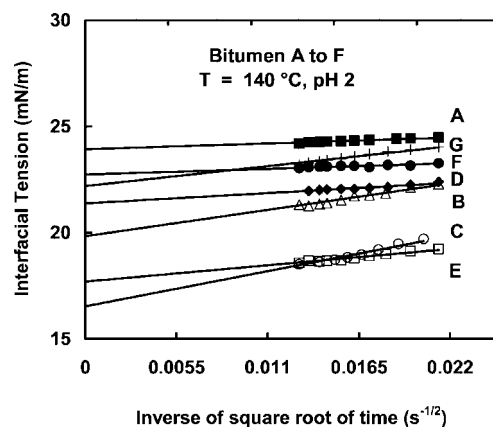


Figure 10. Interfacial tension, γ , between seven different bitumen, labeled “A–G”, and acidified water (pH 2) versus the inverse square root of time. $T = 140\text{ }^{\circ}\text{C}$. The time window is 1900–6900 s. The solid lines are the best fits to a straight line, as expected in the long-time regime.

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Table 4. Analysis of the Time Behavior of the Interfacial Tension, γ , at $T = 140^\circ\text{C}$ and pH 2

bitumen	long-time regime		γ_0 (mN/m)	γ_∞ (mN/m)	$\Delta\gamma = \gamma_0 - \gamma_\infty$ (mN/m)
	time interval (s)	slope from the fit (mN/m/s ^{-1/2})			
C	2000–6000	147.1	24.3	16.6	7.7
D	2000–6000	70.3	24.4	21.4	3.0
F	2000–6000	25.8	24.7	22.7	2.0
G	2000–6000	79.9	25.6	22.3	3.3
estimated error		± 10	± 0.5	± 0.5	± 1.0

characteristic parameters of the adsorption process can be estimated by using the information collected at 90°C . For instance, the γ_0 value at 140°C can be extrapolated from the γ_0 value at 90°C , using the temperature dependence $d\gamma_\infty/dT = 0.24 \pm 0.02 \text{ mN m}^{-1} \text{ }^\circ\text{C}^{-1}$ measured for γ_∞ at 90 and 140°C . Drehlich and Miller²¹ have mentioned a comparable value of $0.10 \text{ mN m}^{-1} \text{ }^\circ\text{C}^{-1}$ for Athabasca sand-extracted bitumen in the temperature range of $23\text{--}50^\circ\text{C}$.

To derive an estimate for r or C_b at 140°C , we have tried two different approaches.

In Table 5a, we have assumed that r is identical at both temperatures and we then calculate C_b from the slope value of the long-time regime. Combining eqs 5, 7, and 8, we obtain

$$C_b = N(1/r^3)(3\pi^2\eta/2)(\text{slope of } \Delta\gamma(t)_{\text{LT}})^{-1} \quad (10)$$

The C_b values at 140°C are given in the fourth column of Table 5a.

In Table 5b, we have assumed that C_b is identical at both temperatures and we then calculate r , again using eq 10. The values for r at 140°C are given in the fourth column of Table 5b. Finally, the interfacial tension decrease, $\Delta\gamma = \gamma_0 - \gamma_\infty$, at 140°C is shown in the last column of Table 4.

We observe that the calculated C_b values at 140°C are systematically lower than at 90°C , when r is taken as independent of the temperature. The difference is large, typically by a factor of 5–10 (see fourth and fifth columns of Table 5a). This is surprising because one would expect the aggregated species in bitumen to be more dissociated at the highest temperature. The pool of potentially surface-active molecules should then increase, which is contrary to our experimental findings. On the opposite, when C_b is taken as independent of the temperature, the calculated r values are much more logical. The molecular size of the surface-active species is found to be smaller at 140°C than at 90°C , which is consistent with the dissociation of aggregated species when the temperature is more elevated. The size reduction is typically by a factor of 2 (see the fourth and seventh column of Table 5b).

Using eq 7 allows us to calculate the surface density at equilibrium Γ_{sat} for a close-packed layer. Similarly, using the Einstein equation and the known viscosities of bitumen at 140°C yields the D_T values. These Γ_{sat} and D_T values are reported in the fifth and sixth columns of Table 5b, respectively.

6. Discussion

The decrease of the interfacial tension between the bitumen droplet and the aqueous solution is clearly due to the progressive adsorption of surfactants present in bitumen. On the one hand, we have shown in the above that their molecular characteristics, such as their size, bulk concentration, and surface concentration, can be derived from the time dependence of the interfacial

tension in the framework of a simple Brownian diffusion model toward a dilute (at short times) or saturated (at long times) bitumen–water interface. On the other hand, the precise identification of the endogenous surface-active molecules is not an easy task. Bitumen is a complex material that contains many different chemical species. They are generally classified into four main categories (they are sometimes referred to as solubility classes): saturated paraffins, cyclic naphtho-aromatics, resins, and asphaltenes.^{4,22} The last two components have been recognized as surface-active,^{23–25} and therefore, both are potential contributors to the lowering of the interfacial tension of crude oil bitumen in our experiments.

Our experiments allow us to estimate that the size of the surface-active species is between 0.3 and 0.7 nm at 140°C and between 0.5 and 1.6 nm at 90°C . Of course, it should be emphasized that this is only an average value. Our model is based on the adsorption of a single native surfactant, and this is clearly an oversimplification to describe the chemical complexity of bitumen in which several surface-active molecules may be present simultaneously. Nevertheless, our data are in striking agreement with the most recent views on the structure of the basic asphaltene unit, namely, a polynuclear aromatic sheet surrounded and/or connected by aliphatic and naphthenic moieties. The number of aromatic rings depends upon the bitumen origin. For instance, Zhao et al.²⁶ have reported an average number of 3 rings for Athabasca bitumen and 11 rings for a Nigerian bitumen. Ruiz-Morales and Mullins²⁷ have confirmed this very recently, using a quantitative comparison between the optical adsorption spectrum of dilute asphaltene solutions and detailed molecular orbital calculations for fused ring systems. They found that asphaltene molecules are constituted mostly of 4–10 6-carbon rings in a flat configuration. They were then able to determine precisely the length of the short and long axis of the asphaltene basic unit. They propose values of 0.68 and 0.92 nm, for a 4-ring system, respectively, 0.96 and 11.5 nm for a 7-ring system, and 0.96 and 11.5 nm for a 10-ring system.

Our values are also in agreement with scanning tunneling microscopy images of asphaltene molecules deposited on gold surfaces.²⁸ It is to be emphasized that we have not based our comparison on the data derived from small-angle neutron or X-ray scattering experiments. It is now well-accepted that such data are systematically overestimated because of aggregation phenomena in the solutions. Indeed, the low sensitivity of the scattering techniques imposes to work at large concentrations, typically in the range of 3–100 mg/mL. Under such conditions, the measured values for the radii of gyration values published in the literature are 3–5 nm^{26,29,30} and correspond to molecular aggregates, even in a good solvent, such as toluene. Similarly, the apparent molecular weight can be as high as 8000 Da when the concentration exceeds a few tenths of a milligram per

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Table 5. Characteristic Parameters of the Endogenous Surfactants at $T = 140\text{ }^{\circ}\text{C}$ and pH 2

assumption 1						
bitumen	slope of LT (mN/m/s ^{-1/2})	<i>r</i> (at 90 °C) (nm)	C _b [10 ⁻¹ (mol/m ³)]	C _b (at 90 °C) [10 ⁻¹ (mol/m ³)]		
C	147.1	0.51 (±10%)	0.44 (±35%)	2.2 (±35%)		
D	70.3	1.1 (±50%)	0.06 (±180%)	0.60 (±180%)		
F	25.8	0.72 (±20%)	0.76 (±70%)	1.3 (±80%)		
G	79.9	0.93 (±40%)	0.10 (±140%)	0.65 (±180%)		
estimated error	±10	see Table 3		see Table 3		
assumption 2						
bitumen	slope of LT (mN/m/s ^{1/2})	C _b (at 90 °C) (mol/m ³)	<i>r</i> (nm)	Γ _{sat} [10 ⁻⁶ (mol/m ²)]	<i>D</i> _T [10 ⁻¹³ (m ² /s)]	<i>r</i> (at 90 °C) (nm)
C	147.1	2.2 (±35%)	0.32 (±10%)	5.10 (±20%)	59.0 (±10%)	0.51 (±10%)
D	70.3	0.60 (±180%)	0.58 (±70%)	1.6 (±140%)	33.0 (±70%)	1.1 (±50%)
F	25.8	1.3 (±80%)	0.62 (±20%)	1.40 (±40%)	31.0 (±20%)	0.72 (±20%)
G	79.9	0.65 (±180%)	0.54 (±70%)	1.80 (±140%)	35.0 (±70%)	0.93 (±40%)
estimated error	±10	see Table 3				see Table 3

milliliter^{11,20,31,32} but drops to about 700 Da at a concentration of 10^{-5} mg/mL.³³ Clearly, the observation of the “basic” asphaltene unit requires working at extremely low concentrations. In their interesting study, Agrawala and Yarranton³³ point out that asphaltenes contain multiple active functional groups capable of linking with other asphaltenes. They view asphaltene association as analogous to linear polymerization, and their model describes satisfactorily the reported dependence of the molar mass distribution on the asphaltene concentration in solution.

Because the present experiments have been performed at pH 2, we can also say that the surface-active species are of basic rather than acidic character. Indeed, acidic groups bearing molecules are not dissociated at this low pH and, consequently, have a lower affinity for the bitumen–water interface than ionized molecules (by the same argument, the influence of molecules bearing neutral groups can be neglected at pH 2). This conclusion is well-supported by our experiments. In Figure 11, for instance, the bitumen with the highest acid index (bitumen D) has the lowest interfacial activity. In contrast, the bitumen with the lowest acid index (bitumen C) shows the highest interfacial activity. More generally, the amplitude of the interfacial tension lowering varies inversely to the acid index value, and this behavior is observed at both 90 and 140 $^{\circ}\text{C}$. In Figure 12, one also observes that the bulk concentration of surface-active species, C_b , that can be deduced from our experiments decreases by more than 10 times when the bitumen acid index increases from 0 to 4.

Asphaltenes possess a large variety of heteroatoms, especially sulfur, nitrogen, and oxygen, that form either acidic (sulfuric or carboxylic) groups or basic (amine) groups.^{5,8,34–37} Consequently, one of their groups will always be ionized and constitute the polar groups necessary for the adsorption on the bitumen–water interface at any given pH. There is a large body of evidence that asphaltenes readily form monolayers at oil–water and air–water interfaces under various pH conditions and with

surface coverage of a few mg m^{-2} .^{24,38,34,39} This yields an estimate of 1.8–3 nm^2 for the molecular cross-section of the asphaltene unit and a corresponding size of 1–1.3 nm.^{11,20,40} Asphaltenes can also be spread directly on the surface of free water using volatile solvents.^{11,23,41}

According to Verhasselt,⁴² as many as 30% of the asphaltenes bear basic groups, whereas resins predominantly bear acidic polar groups. This gives a hint that asphaltenes are the most likely source of surface-active molecules in our experiments. However, it would be premature to infer that resins play no role from a single reference. To address this question more precisely would require measuring the basic nitrogen content of asphaltenes versus resins in the bitumen samples investigated.

The decreases in interfacial tension, $\Delta\gamma = \gamma_0 - \gamma_{\infty}$, that we have obtained are consistent with those previously published for dilute solutions of asphaltenes. For instance, Yarranton et al.²⁰ have investigated the interface tension between water and toluene over a large range of asphaltene concentrations (0.005–50 mol^{-3}). At the highest concentration, the decrease is 10 mN m^{-1} . This is very similar to our own results that show decreases between 2 and 10 mN m^{-1} , depending upon bitumen. For saturated asphaltene films spread directly on water, a paper by Acevedo et al.⁴³ gave values on the order of 20 mN m^{-1} .

One important finding of our experiments is that only a small fraction of the asphaltenes present in bitumen is surface-active. Our results show that the bulk concentration, C_b , of such species is comprised between 2.4×10^{-2} and 2.2×10^{-1} mol m^{-3} at 90 $^{\circ}\text{C}$, whereas the total asphaltene concentration measured by the hexane precipitation method is 10% (w/w), corresponding to 150 mol m^{-3} for a molecular weight of 700. It thus appears that no more than 0.015% of the asphaltenes contribute to the lowering of the interfacial tension. Asphaltene is a generic word that does not describe a single component but rather covers a large variety of molecules. It would be dangerous to try to predict the interfacial properties of bitumen, just knowing its global asphaltene content. For instance, it is said in the literature that each asphaltene unit contains one nitrogen atom and one oxygen atom, on average. However,

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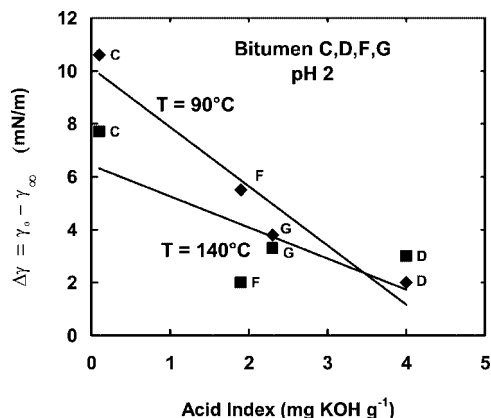


Figure 11. Amplitude of the interfacial tension decrease at long times, $\Delta\gamma = \gamma_0 - \gamma_\infty$, versus bitumen acid index (AI) in milligrams of KOH per gram. Data are for bitumen labeled “C”, “D”, “F”, and “G” at two different temperatures, $T = 90$ and 140 °C.

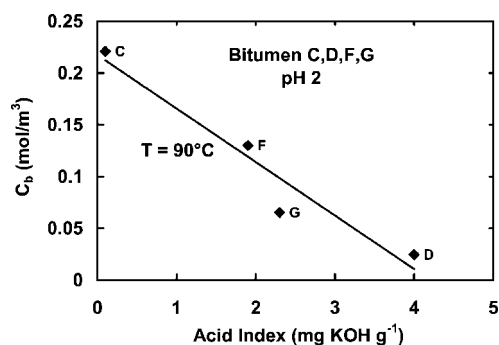


Figure 12. Estimated bulk concentration, C_b , of endogenous surfactants in bitumen “C”, “D”, “F”, and “G” versus bitumen acid index (AI) in milligrams of KOH per gram. Bitumen is in contact with acidified water at pH 2. $T = 90$ °C.

the required number of polar groups to make the molecule surface-active may be much higher, and we surmise that only a small fraction of the asphaltenes fulfills this condition. It would be interesting to collect the interfacial layer and see if its atomic composition is different from the average. This could be achieved by freezing the bitumen droplet after it has been equilibrated with the aqueous phase and analyzing its extreme surface by a high-resolution surface technique, such as X-ray photoelectron spectroscopy. Finally, our observation that only a minute fraction of the asphaltenes is surface-active explains why they have eluded a detailed investigation thus far. It is extremely difficult to isolate them

from the rest of the asphaltenes present in bitumen by classical separation techniques.

7. Conclusions

In this paper, we have investigated seven bitumen of different origins and compositions and observed that they all contain significant amounts of endogenous surfactants. As these surfactants migrate from the bulk to the water interface, the interfacial tension of aqueous-based emulsion droplets is significantly reduced. The adsorption kinetics can be satisfactorily described by a simple diffusion model, assuming a full interface at short times and a crowded one at long times. This is especially true at low temperatures, for which the large viscosity of bitumen slows the kinetics.

When the short- and long-time behaviors are combined, we determined that the surface concentration of molecules adsorbed on the interface at pH 2 range from 1.9×10^{-7} to 2.0×10^{-6} mol m⁻², depending upon bitumen origin. If one assumes close-packed coverage, the typical size and bulk concentration of these endogenous surfactants are estimated to be 0.95 ± 0.5 nm and between 2×10^{-1} and 2×10^{-2} mol m⁻³, respectively.

On the basis of these results and the fact that asphaltenes are known to possess significant amounts of basic groups that ensure good interfacial activity at acidic pH values, we argue that asphaltenes are the most likely source in our experimental conditions. Quite remarkably, we observe that the surface-active species represent only a very small fraction of the total asphaltenes present in bitumen.

This is the first time that quantitative information on endogenous surfactants has been derived without altering the bitumen integrity. Monitoring the adsorption dynamics by the pendent drop technique thus appears as a powerful method to derive the characteristics of surface-active species present in bitumen.

Lastly, because the equilibrium value of the interfacial tension is in the same range as the ones obtained by adding commercial surfactants to the aqueous phase, we suggest that endogenous surfactants could be used as cost-effective substitutes in industrial emulsification of bitumen.

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