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Sulfur Chemistry of Asphaltenes from a Highly Compositionally Graded Oil Column

Andrew E. Pomerantz,*,[†] Douglas J. Seifert,[‡] Kyle D. Bake,[†] Paul R. Craddock,[†] Oliver C. Mullins,[†] Brian G. Kodalen,[§] Sudipa Mitra-Kirtley,[§] and Trudy B. Bolin[∥]

[†]Schlumberger-Doll Research, Cambridge, Massachusetts 02139, United States
[‡]Saudi Aramco, Dhahran 31311, Saudi Arabia
[§]Rose-Hulman Institute of Technology, Terre Haute, Indiana 47803, United States
[∥]Argonne National Laboratory, Argonne, Illinois 60439, United States

ABSTRACT: Hydrocarbons in subsurface reservoirs are generally found to be compositionally graded, with fluids deeper in connected and equilibrated reservoirs being relatively enriched in asphaltenes. These gradients result from effects such as gravity, entropy, and solubility. However, it is unclear if those same effects lead to gradients in the detailed molecular composition of asphaltenes. Here, we investigate the sulfur chemistry of asphaltenes from a reservoir with a large gradient in asphaltene content. Measurements of the sulfur content from combustion as well as measurements of sulfur speciation from K-edge X-ray absorption near edge structure (XANES) spectroscopy find no significant difference in the composition of the asphaltenes. Thus, different locations within this reservoir contain oils with different asphaltene concentrations, but the asphaltenes from throughout the reservoir all have the same sulfur chemistry. This result suggests that gradients in asphaltene content can be successfully modeled with the simplifying assumption that the asphaltene molecular composition is not graded in connected and equilibrated reservoirs.

■ INTRODUCTION

Spatial gradients in the composition of fluids in a hydrocarbon reservoir are routinely observed, with relative enrichment of light ends toward the top of the column and asphaltenes toward the bottom of the column now considered the rule rather than the exception in connected and equilibrated reservoirs.[1] Observed gradients in the light ends are well-modeled by cubic equations of state, such as the Peng−Robinson equation, and more recent models, such as the Flory−Huggins−Zuo (FHZ) equation, are able to capture gradients in the concentration of asphaltenes.[2,3] These fluid gradients can be used to assess reservoir flow connectivity, with certain advantages over traditional methods, such a petrophysical logs and pressure surveys.[4−7] Additionally, fluid compositional gradients are being used to address viscosity gradients, tar mat occurrence, and fault block movement.

The FHZ model of the variation of the asphaltene concentration in crude oil as a function of depth in the reservoir is presented below.

$$\frac{\phi_a(h_2)}{\phi_a(h_1)} = \exp\left\{ \frac{v_a g(\rho - \rho_a)(h_2 - h_1)}{RT} \right. $$
$$ + \frac{v_a}{RT}[(\delta_a - \delta)_{h_1}{}^2 - (\delta_a - \delta)_{h_2}{}^2] $$
$$ \left. + \left[\left(\frac{v_a}{v}\right)_{h_2} - \left(\frac{v_a}{v}\right)_{h_1}\right] \right\}$$

The variables ϕ, R, v, δ, T, g, ρ, and h are the volume fraction, universal gas constant, molar volume, solubility parameter, temperature, Earth's gravitational acceleration, density, and depth, respectively. Subscript a denotes the properties of asphaltenes. Subscripts h_1 and h_2 stand for the properties at depths h_1 and h_2, respectively. This equation considers three forces driving asphaltene content gradients, gravity, entropy, and solubility, in the three terms, respectively.[2,3,8] Gravity is typically the dominant force driving asphaltene content gradients in heavier oils, while solubility is typically dominant in lighter oils and entropy is typically a minor factor.

Petroleum is a complex mixture containing such a large number of unique components as to challenge even the most sophisticated analytical instruments.[9,10] Asphaltenes are defined as a solubility-based fraction of petroleum (soluble in aromatic solvents, such as benzene or toluene, and insoluble in aliphatic solvents, such as pentane or heptane). Although recent studies have provided some clarity on the dominant molecular weights and structures in asphaltenes, even this fraction of petroleum is highly complex.[11−21] Previous studies of asphaltene gradients have focused on measuring the content of the entire asphaltene fraction in petroleum, often measured by optical spectroscopy or solvent precipitation.[2,3,5,6,8] However, gradients in the detailed chemical composition of the asphaltene fraction may exist and would not be detected by these methods.

One way to evaluate the chemical composition of asphaltenes is through their sulfur speciation. Sulfur is relevant to many reservoir processes, such as petroleum generation, microbial activity, and thermochemical-sulfate reduction.[22,23] Sulfur in asphaltenes and crude oils can exist in a number of chemical-

bonding environments, such as sulfides (sulfur in an aliphatic chain), thiophenes (sulfur in an aromatic ring), and sulfoxides (sulfur double bonded to oxygen), and the abundance of those groups is related to the above processes.[24−26] Asphaltenes from different basins have been found to differ dramatically in sulfur speciation.[27]

Here, we measure the sulfur speciation in black oils from a Saudi Arabian anticlinal closure. Oils were collected from three wells covering a 700 ft vertical range in two stacked reservoirs. These oils present a large gradient in asphaltene content, from near 2 wt % asphaltenes at the top of the upper reservoir to near 31 wt % asphaltenes at the bottom of the upper reservoir. Thus, one might expect that any gradients in asphaltene composition would be relatively large as well. Sulfur chemistry might be expected to present an especially large gradient, given the role of sulfur in numerous reservoir processes. However, no gradients in sulfur content or speciation are observed. Implications of this result for interpreting gradients in asphaltene content are discussed.

■ EXPERIMENTAL SECTION

Oil Samples. Eight oil samples were taken from a Saudi Arabian anticlinal closure holding a black oil, as described previously.[28−31] Two stacked reservoirs in this structure (referred to as "reservoir A" and "reservoir B") spanning a depth range of 700 ft were sampled with three wells. The collected oils present a large gradient in asphaltene content, as shown in Figure 1, with asphaltene content increasing with
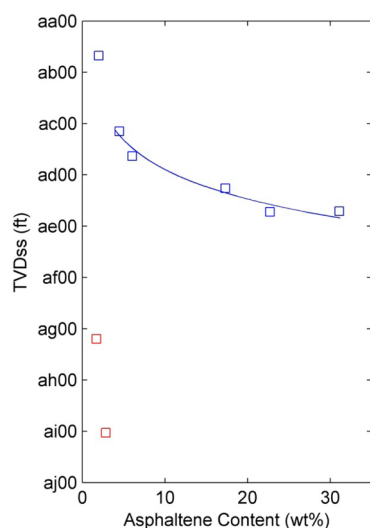

Figure 1. Asphaltene content gradient in reservoirs A (blue) and B (red). The *y* axis represents depth in the reservoir, expressed as true vertical depth subsea (TVDss). The first digits of the depths have been obscured to preserve reservoir anonymity and are not essential for this analysis, which relies only on relative depths. The measured gradient (points) in reservoir A above 4 wt % asphaltenes is well-fit by the FHZ equation of state, including only the gravity term (line).

depth within each reservoir unit. Such gradients are expected for connected reservoirs and predicted by the FHZ equation of state.[2,3] Also shown in Figure 1 is a version of the FHZ model of the asphaltene content for reservoir A, with only the gravity term included in the model. Oils with asphaltene contents exceeding 4 wt % are expected to contain asphaltenes in the form of clusters, and fitting the measured data above 4 wt % to the model returns an asphaltene particle size of 5.1 nm, demonstrating that, in this reservoir, the asphaltenes exist in the form of clusters, as described by the Yen−Mullins model of asphaltenes.[14,28,32]

Asphaltene Analysis. Asphaltenes were isolated from the crude oils for compositional analysis. The asphaltenes were extracted using the standard precipitation procedure with *n*-pentane. Briefly, the oils were mixed 1:40 with *n*-pentane and stirred overnight. The solutions were then vacuum-filtered, and the precipitates were washed with excess *n*-pentane until the rinse ran clear and colorless.

Sulfur speciation in the asphaltenes was measured by sulfur K-edge X-ray absorption near edge structure (XANES) spectroscopy. This spectroscopy measures electronic transitions from 1s orbitals on sulfur to vacant molecular orbitals with substantial 3p character.[33] The energy of this transition is a strong function of the oxidation state of sulfur and varies by approximately 10 eV for sulfur in different functional groups.[24,34−39] Figure 2 shows the sulfur XANES spectra of
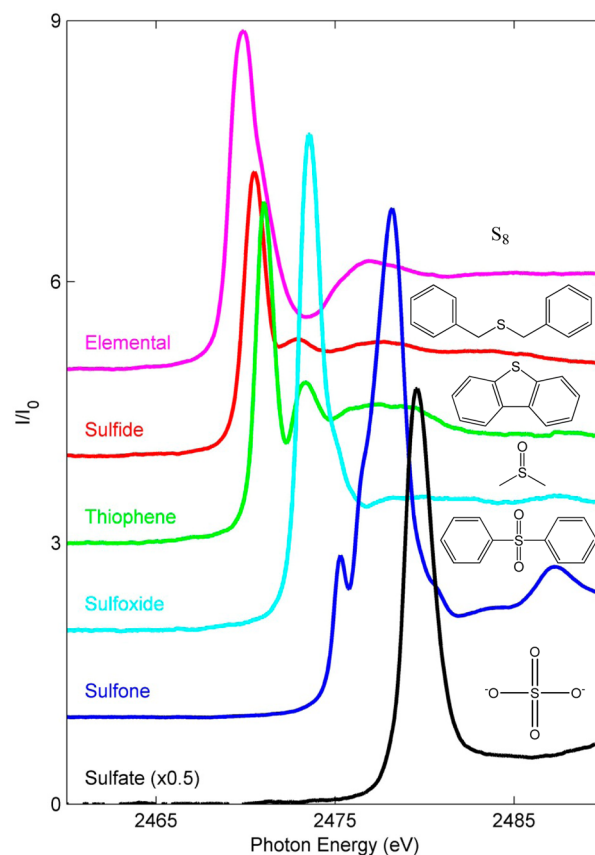

Figure 2. Sulfur K-edge XANES spectra of model compounds (elemental sulfur, benzyl sulfide, dibenzothiophene, dimethyl sulfoxide, phenyl sulfone, and potassium sulfate). The *y* axis shows the normalized fluorescence intensity, and the *x* axis shows the energy of the incident photon.

six model compounds representing sulfur-containing functional groups potentially present in asphaltenes: elemental sulfur, sulfides, thiophenes, sulfoxides, sulfones, and sulfates. The ability of XANES to resolve these functional groups is clear.

XANES measurements were recorded in fluorescence yield mode at the Advanced Photon Source, beamline 9-BM. Details of the analysis procedure are described by Bolin.[40] Spectra are plotted as the ratio of I, the intensity of the total fluorescence signal, to I_0, the intensity of the excitation radiation, as a function of the excitation photon energy. Samples were analyzed in solution phase, diluted to 10 wt % in dichloromethane. The asphaltenes studied here contain less than 10 wt % sulfur (see Figure 5 below); therefore, the analyzed solutions contain no more than 1 wt % sulfur. This method of sample preparation, including limiting the sulfur content of the analyzed solution to below 1 wt %, has been found to minimize self-absorption, resulting in XANES spectra that can be interpreted quantitatively.[41−43]

Measured XANES spectra were baseline-corrected by setting I/I_0 to zero in the pre-edge region (<2465 eV) and normalized by setting I/I_0 to unity in the post-edge region (>2490 eV). The spectra were then fitted to a linear combination of the spectra of the model compounds shown in Figure 2. The fitting weights were taken as proportional to the abundances of the corresponding functional groups in the asphaltene samples.

■ RESULTS AND DISCUSSION

XANES spectra of these asphaltenes are shown in Figure 3. The spectra are nearly identical and contain one dominant peak near
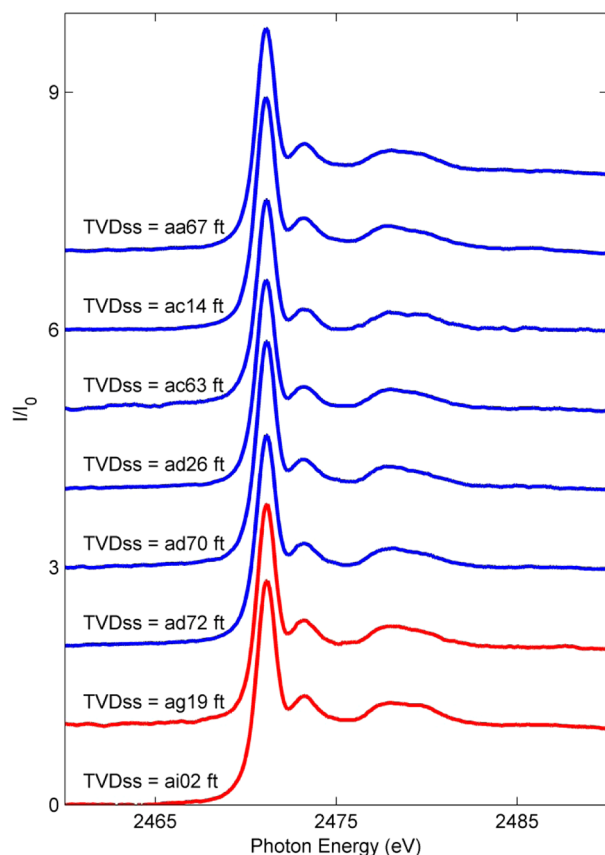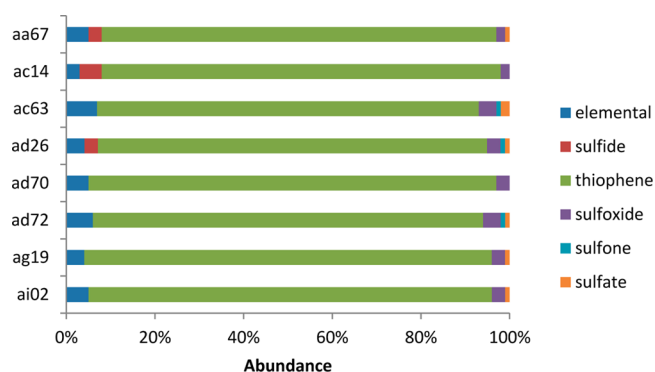

Figure 4. Sulfur speciations derived from fitting the spectra in Figure 3. Asphaltene samples are arranged from shallowest at the top of the plot to deepest at the bottom of the plot, with the depth of each sample labeled as TVDss. The top six asphaltenes come from reservoir A, and the bottom two asphaltenes come from reservoir B. Each asphaltene has essentially identical sulfur speciation, dominated by thiophenes.

Sulfur contents of these asphaltenes as measured by combustion are shown in Figure 5. Again, there is remarkable
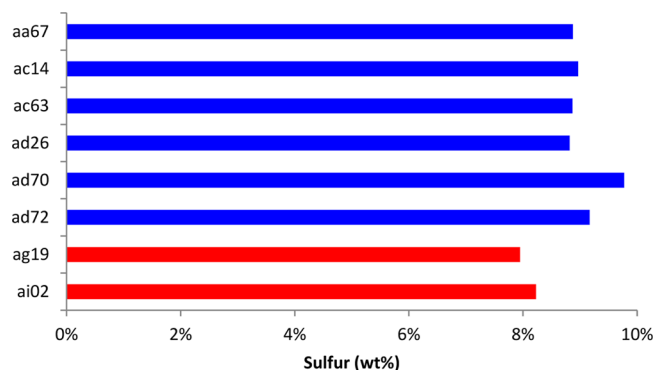

Figure 5. Measured sulfur contents. Asphaltene samples are arranged from shallowest at the top of the plot to deepest at the bottom of the plot, with the depth of each sample labeled as TVDss. Asphaltenes within reservoir A (blue) have identical sulfur content, as do asphaltenes within reservoir B (red). There is a small difference between the A and B asphaltenes, comparable to the experimental uncertainty.

Figure 3. Measured XANES spectra. Spectra of asphaltenes from reservoirs A (blue) and B (red) are nearly identical. Spectra are offset for clarity of presentation and arranged in order of depth (shallowest at the top and deepest at the bottom), with the depth of each sample expressed as TVDss.

2471 eV, the same energy as the peak in the thiophene standard. Not surprisingly, the fitted compositions are nearly identical and show that sulfur in these asphaltenes is found almost exclusively in thiophenes (Figure 4). Thiophenes consist of sulfur in an aromatic carbon ring and are relatively thermally stable. The asphaltene fraction is concentrated in aromatic carbon relative to the whole crude oil, and one might expect that sulfur in asphaltenes is also concentrated in aromatic thiophene moieties. Indeed, it has been observed that thiophenes are often the most abundant form of sulfur in asphaltenes, especially in asphaltenes from mature oils.[24,25] However, asphaltenes from different basins have been found to contain a wide diversity of sulfur speciations often but not exclusively dominated by thiophenes,[44] in stark contrast to the nearly identical speciations observed for these samples.

consistency among the samples. The heteroatom (nitrogen, sulfur, and oxygen) contents of asphaltenes generally sum to approximately 10 wt % or less, although the amounts of nitrogen, sulfur, and oxygen vary considerably within that range.[45] In contrast, here, we find little variation in sulfur content and, in particular, no trend with depth within each reservoir. Between reservoirs A and B, there is a difference in sulfur content of around 1 wt %, comparable to the experimental uncertainty.

These results have significant implications regarding reservoir compositional gradients. Reservoir A contains a large gradient in asphaltene content, and equations of state, such as the FHZ equation, are used to model such gradients.[2,3] According to the FHZ equation, gradients in the composition of reservoir fluids are controlled by three dominant forces: gravity, entropy, and solubility. For some black oil and most heavy oils, including the fluids studied here, asphaltenes exist mainly as clusters in the Yen−Mullins classification.[14,28,32] Because the asphaltenes reside in relatively large particles, the density contrast between

the asphaltenes and the rest of the hydrocarbon fluid is emphasized. The emphasized density contrast leads to stronger gravitational segregation, and gradients in asphaltene concentration for black oils and heavy oils, including these fluids, are driven mostly by the effect of gravity.

Although it is now understood how the forces of gravity, entropy, and solubility lead to gradients in the amount of asphaltenes in crude oil at different depths, it is unclear if these forces also lead to gradients in the detailed chemical composition of asphaltenes at different depths; undoubtedly, there are more asphaltenes in oils from deeper in the reservoir, but whether the chemistry of the asphaltenes from higher in the reservoir is similar or different from the chemistry of asphaltenes from lower in the reservoir is unproven. Here, we find remarkable consistency in the sulfur content and speciation in asphaltenes. Even though the effect of gravity has caused a strong gradient in the amount of asphaltenes in the petroleum at different depths, there appear to be no differences in the sulfur chemistry of asphaltenes from different depths.

This observation that the chemical compositions of the asphaltenes from all locations in the connected reservoir are similar suggests that the asphaltene clusters formed in the oil are essentially identical within the reservoir unit. If, for example, thiophene-containing asphaltenes preferentially formed clusters of different particle size than nonthiophene-containing asphaltenes, then the effect of gravity on the two different clusters would be different and gradients in the asphaltene sulfur content and/or composition would be expected. No such gradients are detected, implying that deeper locations contain merely more asphaltene than shallower locations and not different asphaltenes.

Between reservoirs A and B, the sulfur speciation of the asphaltenes is identical within experimental uncertainty and the sulfur content of the asphaltenes differs by an amount equal to the experimental uncertainty. These two stacked reservoirs have the same source rock and similar charge histories, and neither is affected by biodegradation. Thus, general similarity between these oils is expected, as is found here. Both of these reservoirs show gradients of asphaltene content driven by gravitational segregation, but in neither case does gravity result in a gradient of asphaltene composition.

CONCLUSION

Eight oils spanning two stacked reservoirs covering a 700 ft vertical range from three wells are studied regarding their asphaltene content and asphaltene sulfur chemistry. These oils, in particular the six oils from the upper reservoir, present a massive gradient in asphaltene content (from 2 to 31 wt %) that can be modeled by the effect of gravity, as described in the FHZ equation. The sulfur chemistry of the asphaltene fractions of these oils is measured by combustion to determine the total sulfur content and by XANES to measure the relative abundance of sulfur-containing functional groups. No variations in sulfur content or speciation are found among the asphaltenes within either reservoir, suggesting that gravitational effects lead to variation in the asphaltene content within a reservoir but do not lead to variation in the composition of asphaltenes within a reservoir.

Equations of state, such as the FHZ equation, are capable of modeling gradients in asphaltene content, and in this study, the gravity term in the FHZ equation (with one tightly constrained variable) was found to successfully model the asphaltene content gradient. The FHZ equation relies on the assumption that only the asphaltene content is graded and, in particular, that the composition of the asphaltenes is constant throughout a connected and equilibrated reservoir unit. However, that assumption has not been previously tested, because measurements of asphaltene content, such as optical spectroscopy or solvent precipitation, are not very sensitive to variations in the molecular composition of asphaltenes. The data presented here represent the first rigorous test of this assumption, and the data are consistent with the assumption being valid; different locations within these connected and equilibrated reservoirs contain oils of different asphaltene concentrations, but those asphaltenes have similar sulfur chemistries. This result suggests that the FHZ equation can indeed be used to interpret asphaltene gradients accurately, even in reservoirs such as these examples with extreme compositional gradients. At the same time, we note that the chemical composition of asphaltenes is complex, and measurements of the sulfur chemistry as reported here do not capture all possible variations in asphaltene molecular composition. Future work will probe other aspects of the composition of these asphaltenes, such as molecular weight and carbon structure, in an attempt to constrain further any similarity or dissimilarity in the chemical composition of asphaltenes within a reservoir unit.

AUTHOR INFORMATION

Corresponding Author
*E-mail: apomerantz@slb.com.

Notes
The authors declare no competing financial interest.

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