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Role of Naphthenic Acids in Emulsion Tightness for a Low Total Acid Number (TAN)/High Asphaltenes Oil: Characterization of the Interfacial Chemistry[†]

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The detailed composition of a low total acid number (TAN) crude oil that causes unusually severe water–oil emulsion problems along the production stream was studied by Fourier transform ion cyclotron resonance mass spectrometry and infrared spectroscopy. Distinct fractions, such as asphaltenes, whole interfacial material, extracts from the interfacial material, etc., were prepared for characterization. The detailed compositional analysis of the interfacial material showed the predominance of asphaltenes together with high amounts of distinctive mono- and diprotic naphthenic acids and sulfur- and oxygen-containing aromatic molecules. In addition, the interface was found to be heterogeneous. A primary group of species that is strongly bonded to the water surface consists of fatty monoprotic acids, fatty, naphthenic, and aromatic diprotic acids, and some alkyl benzene sulfonates. A secondary part of interfacial material consists of various classical asphaltene-related components, such as aromatic sulfur–oxygen-containing species, together with naphthenic and aromatic monoprotic acids. This paper focuses on the analytical part of a larger study of the particular tight water–oil emulsion of this Arabian crude oil. The other two parts of this study address rheological and other physical approaches to investigate this water–oil emulsion.

Introduction

The formation of a water–oil emulsion can be a serious obstacle for the production of crude oil, and some oils are particularly prone to form tighter emulsions than others. Phenomenological investigations of the physical and chemical properties related to emulsion tightness are described in the literature in terms of mechanisms, properties, and potential compound classes that stabilize emulsions.^{1–4} Of the most noteworthy bulk properties commonly connected to water–oil emulsions are gravity (API), total acid number (TAN), and asphaltene content. Several studies focused on physical methods to study the rheology of the interface.^{1–4} Recent developments, however, suggested that more detailed investigations on the molecular level are beneficial for further understanding of emulsion phenomena and helping in classifying and predicting water–oil emulsions.^{5–8}

Various recent studies focused on the characterization of the molecular species in oil deposits or emulsions to identify the

responsible species. This more direct approach studies the chemical composition of the material that particularly stabilizes the water–oil interface.^{6–8} In these studies, high-resolution mass spectrometry has been proven an especially useful tool to reveal detailed chemical information and help with the characterization of complex hydrocarbon mixtures in, otherwise, unapproachable complex samples. High-resolution Fourier transform ion cyclotron resonance mass spectrometry (FT–ICR–MS) has been extensively used for the characterization of organic acids that are a prime suspect in any emulsion study.^{6–8} In this paper, we will focus on the characterization of the interfacial material isolated from the tight water–oil emulsion of a low TAN Arabian crude oil (TAN below 0.25 mg of potassium hydroxide) with comparably high asphaltene content. It is the third part of a series of papers that study the role of naphthenic acids in stabilizing a particularly tight water–oil emulsion of this oil. The chemical composition of the isolated interfacial material is characterized using high-resolution Fourier transform mass spectrometry and infrared (IR) spectroscopy. The other two parts^{9,10} of this study combine rheological and physical aspects to discuss the emulsion tightness of the studied oil.

Experimental Section

Sampling and Sample Preparation. The samples were collected at atmospheric pressure before the gas oil separator plant. The oil samples contained no free water because all of the water was dispersed in the form of an emulsion. Samples were stored for several days, during which the initial emulsion aged and settled

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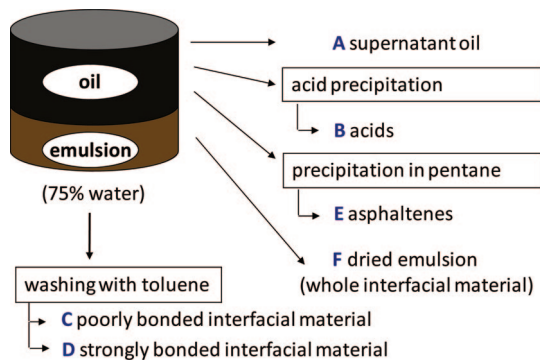


Figure 1. Illustration of the sample preparation scheme for the preparation of (A) crude oil, (B) acids, (C) poorly bonded interfacial material, (D) strongly bonded interfacial material, (E) asphaltenes, and (F) the dried emulsion, which represents the whole interfacial material.

down. This sludge-like emulsion was then isolated and is referred to as whole interfacial material (F). It was then directly analyzed by IR spectroscopy or further fractionated according to the scheme presented in Figure 1. It is noteworthy to mention that the whole interfacial material (F) also contains some entrapped oil. For the fractionation, the emulsion was repeatedly washed by vigorous mixing with toluene followed by settling of the emulsion layer. This washing step was repeated 10 times until the supernatant solvent was clear. The combined toluene phases of the washing steps (further referred to as the poorly bonded interfacial material, C) contained the desorbed interfacial material and some entrapped oil. This fraction was characterized by FT-ICR-MS and IR spectroscopy and for asphaltenes content.

The strongly bonded interfacial material (D) was obtained as an almost colorless material, consisting of the strongly bonded interfacial species and up to 75 wt % water. This emulsion was then further dried or digested with a strong acid. For the acid digestion, the method described by Mediaas for naphthenate deposits¹¹ was followed. A sample of toluene-extracted emulsion was shaken in large volumes of hydrochloric acid (1 M) and toluene for 24 h. The released species were collected in the toluene phase. Organic acids (B) in Figure 1 were isolated by a modified extraction procedure.¹² The asphaltenes (E) were prepared by precipitation from pentane at a ratio of 1 g of oil to 40 mL of pentane, and the precipitated asphaltenes were dried and weighed.

IR Spectroscopy. Fourier transformed IR spectroscopy was used for characterizing the functional groups present in the molecules in a sample. Each functional group will absorb IR photons at a range of wavenumbers (bands). Identification of sample components can be difficult because of overlapping or shifting adsorption bands of different functional groups depending upon the sample composition and the structure of the molecules. This can be particularly true for vastly complex crude oil samples. IR spectroscopy, therefore, provides a coarse but fast overview on the averaged functional groups present in all of the molecules in a sample. In contrast to the analysis of the bulk petroleum samples, IR spectroscopy can reveal distinctive structural features when clearly defined subfractions are analyzed. Despite these drawbacks, IR spectroscopy has been widely used for characterizing various petroleum components, especially acids,^{13,14} asphaltenes,¹⁵ and interfacial materials.^{16–18}

For this study, IR spectra were acquired in transmission mode on a Nicolet Magna 860 spectrophotometer with a Spectratech 0002-

391 diffuse reflectance infrared (DRIFT) accessory. The recorded wavenumber range was 500–4500 cm^{-1} , with a resolution of 8 cm^{-1} . Samples were thoroughly mixed with highly pure potassium bromide, loaded into the sample holder, and then analyzed against a potassium bromide background. Samples initially containing water (sludge emulsion or cleaned emulsions) had been dried for at least 12 h under a heating lamp prior to measurements.

FT-ICR-MS. While IR spectroscopy provides the averaged functionalities of all of the molecules in an analyzed fraction, ultra-high-resolution FT-ICR-MS can be used to obtain a deeper insight into individual structural features of the species. Oxygen-, nitrogen-, and sulfur-containing molecules are believed to contribute in different degrees to the water–oil emulsion stability. In this study, electrospray ionization (ESI) was applied in the negative mode to yield preferentially ions of acidic species (that are susceptible to deprotonation) to characterize these species in different emulsion-related fractions.¹⁹ Mass spectra were acquired at the National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL, on a custom-built FT-ICR mass spectrometer,¹⁹ equipped with a 9.4 T superconducting magnet.^{20,21} The experimental conditions have been reported previously^{8,19–23} for the characterization of heteroatom compounds in petroleum samples.

Ultra-high mass resolution ($R > 300\,000$) and a resolving power high enough for separating signals spaced as closely as 1.1 mDa (SH_3^{13}C versus $^{12}\text{C}_4$) are essential for the correct assignment of elemental compositions ($\text{C}_x\text{H}_y\text{N}_z\text{O}_w\text{S}_w$) for complex samples, such as crude oils. Using internal mass calibrants, the data are recorded with sufficient precision and mass accuracy to assign a unique elemental composition to each mass signal in the spectrum. The identified species are then classified according to the heteroatoms in the elemental composition, e.g., none = pure hydrocarbons, one oxygen (or nitrogen) atom per molecule = mono-oxygen (or mono-nitrogen) species, or molecules with a combination of heteroatoms. The elemental compositions were provided from Florida State University as raw data for interpretation. The corresponding double-bond equivalent (DBE) and carbon number were calculated for each identified signal, where the DBE is defined as the number of hydrogen atoms lacking from an elemental composition in comparison to the corresponding saturated molecule with an otherwise identical number of carbon and heteroatoms. Every ring or double bond in a molecule reduces the number of hydrogen atoms by two. For example, hexane is fully saturated without a ring and has a DBE of zero. Cyclohexane contains one ring and hence features a DBE of one. Benzene features one ring and three double bonds and hence has a DBE value of four. The DBE values are plotted versus carbon numbers for the following discussion.²³ In this type of graph, data points with higher DBE values represent molecules with a higher degree of unsaturation and dots at larger carbon numbers represent larger molecular size. The relative intensity of each mass signal is represented by the size of its corresponding data point. Intensities between two heteroatom classes (plots) cannot be compared because of their unknown response factors. The data

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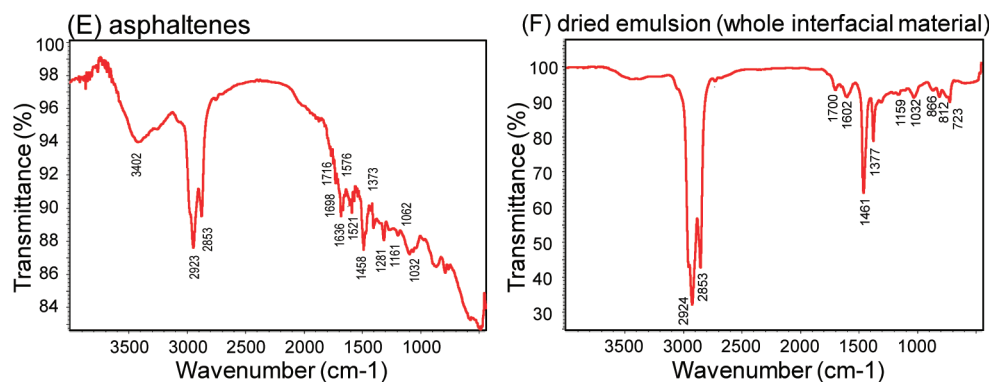


Figure 2. FTIR spectra of the (E) (left) asphaltenes and (F) (right) dried emulsion.

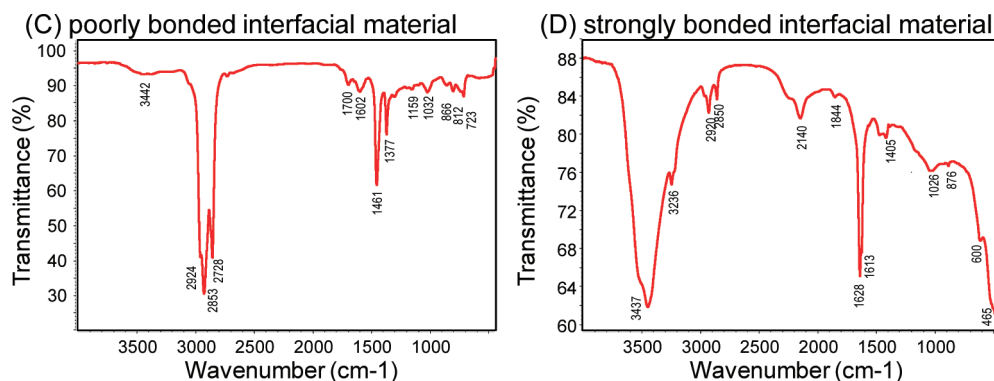


Figure 3. IR spectra of the (C) (left) poorly bonded interfacial material and (D) (right) the strongly bonded interfacial material.

within one class (plot) are semi-quantitative, and the relative intensities (data point sizes) can be compared.

Results

Fourier Transform IR Spectroscopy. Figure 2 displays the IR spectra obtained from the whole interfacial material (F) and from the asphaltene fraction of the same oil (E), respectively.

Both spectra in parts E and F of Figure 2 show similar features and contain characteristic bands for aliphatic, aromatic, and carboxyl functions.²⁴ An aliphatic signature is indicated at 2920, 2850, 1460, and 1376 cm⁻¹. The IR band around 1700 cm⁻¹ and between 1630 and 1600 cm⁻¹ could be associated with carboxylic acid functions by comparison to the spectrum of sodium tartrate. Bands from 1600 to 1500 cm⁻¹ and the numerous signals below 900 cm⁻¹ are an indication of aromatic rings. Bands at 1161, 1062, and 1032 cm⁻¹ could indicate sulfonates, sulfones, or sulfoxides functions in the molecules.²⁵ The broad band at 3402 cm⁻¹ may be attributed to residual water in the asphaltene sample. The relatively high intensity of the aliphatic bands exhibited by the spectrum of the whole interfacial material can probably be attributed to the presence of oil entrained in the emulsion. This interpretation is also supported by the FT-ICR-MS data presented below.

In comparison, the IR spectra obtained for the poorly bonded interfacial material in Figure 3C and for the strongly bonded interfacial material in Figure 3D are quite different. The spectrum of the poorly bonded interfacial material (C) is very similar to the one of the untreated emulsion and the one obtained for the asphaltenes shown in parts E and F of Figure 2. The

spectrum of the strongly bonded interfacial material in Figure 3D matches that of a tartrate salt with a weakly overlaid signature of asphaltenes: the distinctive bands at 1628 and 1405 cm⁻¹ match the symmetric and asymmetric stretch of a deprotonated carboxylic acid function (COO⁻) as observed for tartrate salts. The broad band around 3500 cm⁻¹ in both spectra may result from residual water or hydroxyl groups present in the samples. A comparison of the IR spectra in Figures 2E and 3C suggests that the asphaltene fraction of the oil contains molecules with similar functions to the toluene-soluble part of the emulsion.

Washing the emulsion with toluene removes or reduces the features that are characteristic for asphaltenes and the whole interfacial material, but a distinctive signature of carboxylic acid functions appear in the corresponding spectrum in Figure 3D. In conclusion, asphaltene-like species are removed from the interface by washing with toluene while carboxylic acids are being enriched. An IR absorption band at 2140 cm⁻¹ in the spectrum in Figure 3D could further indicate the presence of sulfoxides, sulfones, or sulfonates in the strongly bonded interfacial material.

FT-ICR-MS. ESI FT-ICR-MS was used in the negative mode to identify acidic species (that are susceptible to deprotonation) in the crude oil (A), extracted acids (B), and poorly (C) and strongly (D) bonded interfacial material. Oxygen-sulfur- and oxygen-containing species were found with the highest abundances in the interfacial material and are, therefore, most important for understanding the emulsion behavior of the investigated oil. The following results for the most abundant heteroatom classes were obtained and are now presented in the form of DBE versus carbon number plots:

Tri-oxygen-sulfur (O₃S) Species. Several series of tri-oxygen sulfur (O₃S) species are identified in the crude oil (Figure 4A). When the data sets obtained for the crude oil are compared to those of the acidic extract shown in Figure 4B, it is evident

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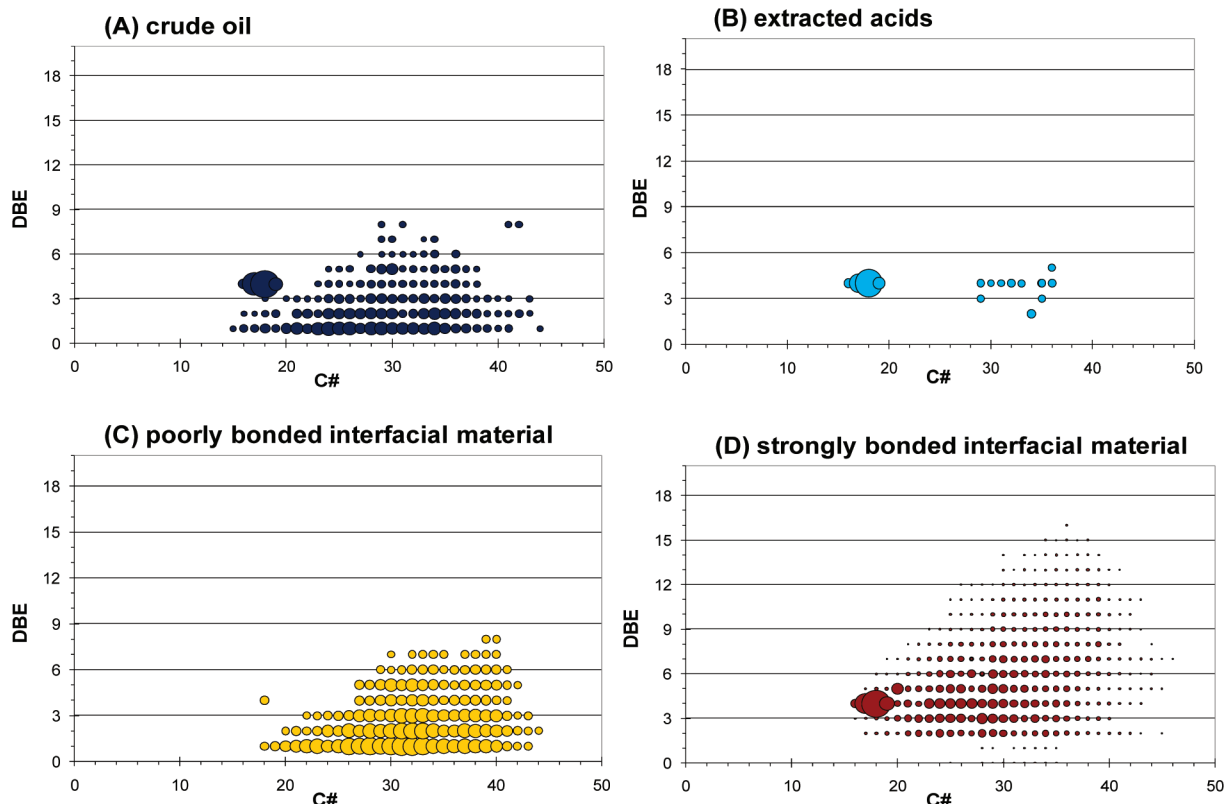


Figure 4. DBE versus carbon number plots for all species that contain one sulfur and three oxygen atoms per molecule (O_3S species) in the (A) crude oil (upper left), (B) acid extract (upper right), and for the (C) poorly bonded interfacial material (lower left) and (D) strongly bonded interfacial material (lower right).

that only a few O_3S species in the oil contain acidic functions. The plot of the strongly bonded interfacial material in Figure 4D shows the largest number of O_3S species, with DBE values above 1 and carbon numbers ranging from 16 to 40, and extending up to about 15 rings/double bonds per molecule. The data for the poorly bonded interfacial material Figure 4C have a somewhat similar carbon range but lower DBE values, ranging from 1 to 8. The O_3S species seem to be enriched at the interface and strongly bonded because they have not been removed by the toluene extraction. O_3S species with a higher degree of unsaturation (higher DBE values) seem to be enriched at the interface, whereas those O_3S species with a higher degree of saturation (lower DBE values) seem preferentially removed by the toluene extraction.

A distinctive group of three O_3S species (C_{17-19} and DBE = 4) is present in the data sets for crude oil, acids, and strongly bonded interfacial material in parts A, B, and D of Figure 4, respectively. These are characteristic features for alkyl benzene sulfonates with 11–13 alkyl carbon atoms. Alkyl benzene sulfonates are oilfield chemicals commonly used as asphaltene controllers, detergents, and fouling control additives.^{4,13} These chemicals have likely been added in the production line upstream of the sampling point. The presence of these highly surface-active components, however, contributed to the stabilization of the interface and is therefore part of the emulsion problem.

Despite the fact that most O_3S species seem not to be acidic, because they are not precipitated by the modified extraction procedure¹² as the carboxylic acids were, they associate closely with the interface. Particularly, O_3S species with higher DBE values seem more strongly bonded to the interface than more saturated ones.

Di-oxygen Sulfur (O_2S) Species. The patterns of O_2S species in the crude oil and the extracted acids are shown in parts A

and B of Figure 5, respectively. Few of the O_2S species are found with a low abundance in the acid extract, indicating the absence of carboxylic acids in this class. The O_2S species in the oil and the poorly bonded interfacial material in parts A and C of Figure 5, respectively, show very similar DBE value and carbon number distributions. No O_2S species are identified in the strongly bonded interfacial material (Figure 5D), which is in agreement with the fact that the O_2S species of this oil seem not to contain acid functions, whereas acidic species seem to be especially attracted to the interface. Most O_2S species are, therefore, not found in the acid extract in contrast to the O_3S species, which are partially found in the acid extract, as can be seen in Figure 4B. The O_2S species are exclusively found in the poorly bonded interfacial material in comparison to the O_3S species.

Oxygen Species. Di-oxygen (O_2) Species. Di-oxygen (O_2) species are the main constituents found after the modified acid precipitation process,¹² as shown in Figure 6B. By comparing the plots obtained for the crude oil and the extracted acids, it appears that almost all O_2 compounds present in the crude oil are carboxylic acids (parts A and B of Figure 6). An identical pattern of these acids in terms of DBE and carbon number distribution can also be seen in the mass data for the poorly bonded interfacial material in Figure 6C. This leads to the conclusion that most monocarboxylic acids are present in the poorly bonded interfacial material, regardless of their molecular weight or degree of saturation. The apparent vertical concentration of O_2 species with DBE values from 6 to 13 around carbon number 39 in parts A and C of Figure 6 indicates an un-identified common structural feature that is currently under investigation. The horizontal group of species at DBE = 1 is observed in all spectra (A–D) and indicates fatty acids with unsaturated alkyl chains. The species with low carbon numbers and high DBE values in the upper left region of the plots (parts

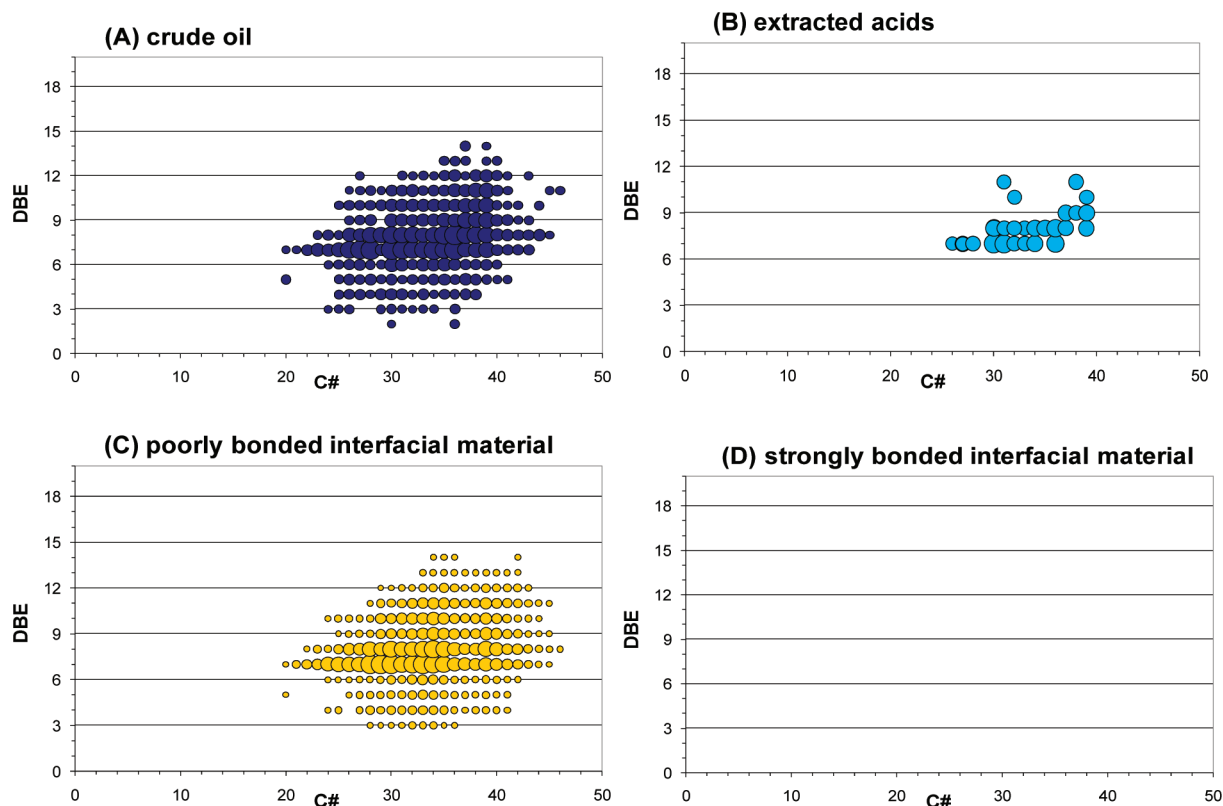


Figure 5. DBE versus carbon number plots for all species that contain one sulfur and two oxygen atoms per molecule (O_2S species) in the (A) crude oil (upper left), (B) acid extract (upper right), and for the (C) poorly bonded interfacial material (lower left) and (D) strongly bonded interfacial material (lower right).

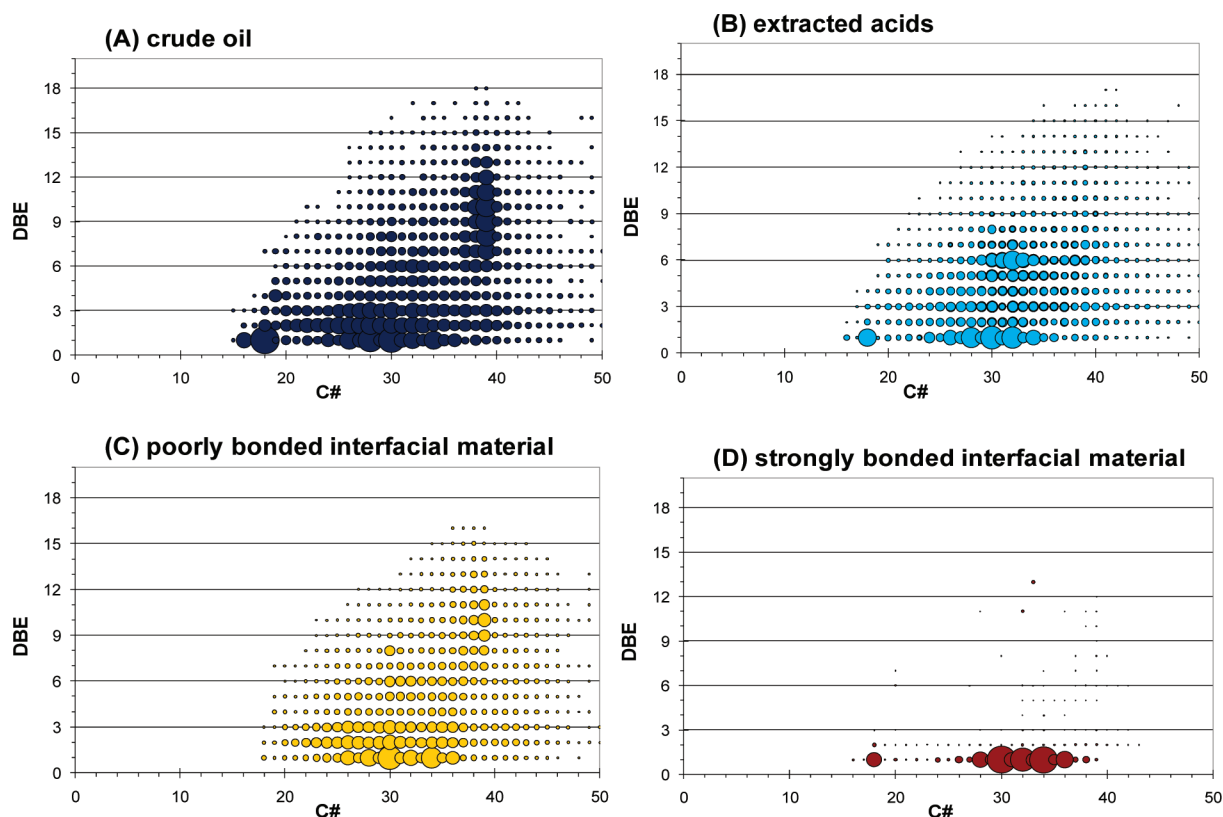


Figure 6. DBE versus carbon number plots for all species that contain two oxygen atoms per molecule (O_2 species) in the (A) crude oil (upper left), (B) acid extract (upper right), and for the (C) poorly bonded interfacial material (lower left) and (D) strongly bonded interfacial material (lower right).

A–C of Figure 6) cannot theoretically be explained by naphthenic (completely saturated) rings alone, because the number of naphthenic rings in a molecule is limited by the

number of carbon atoms. This limits the maximum DBE value for a naphthenic structure. Species with higher DBE values than possible for naphthenic structures must contain one or more

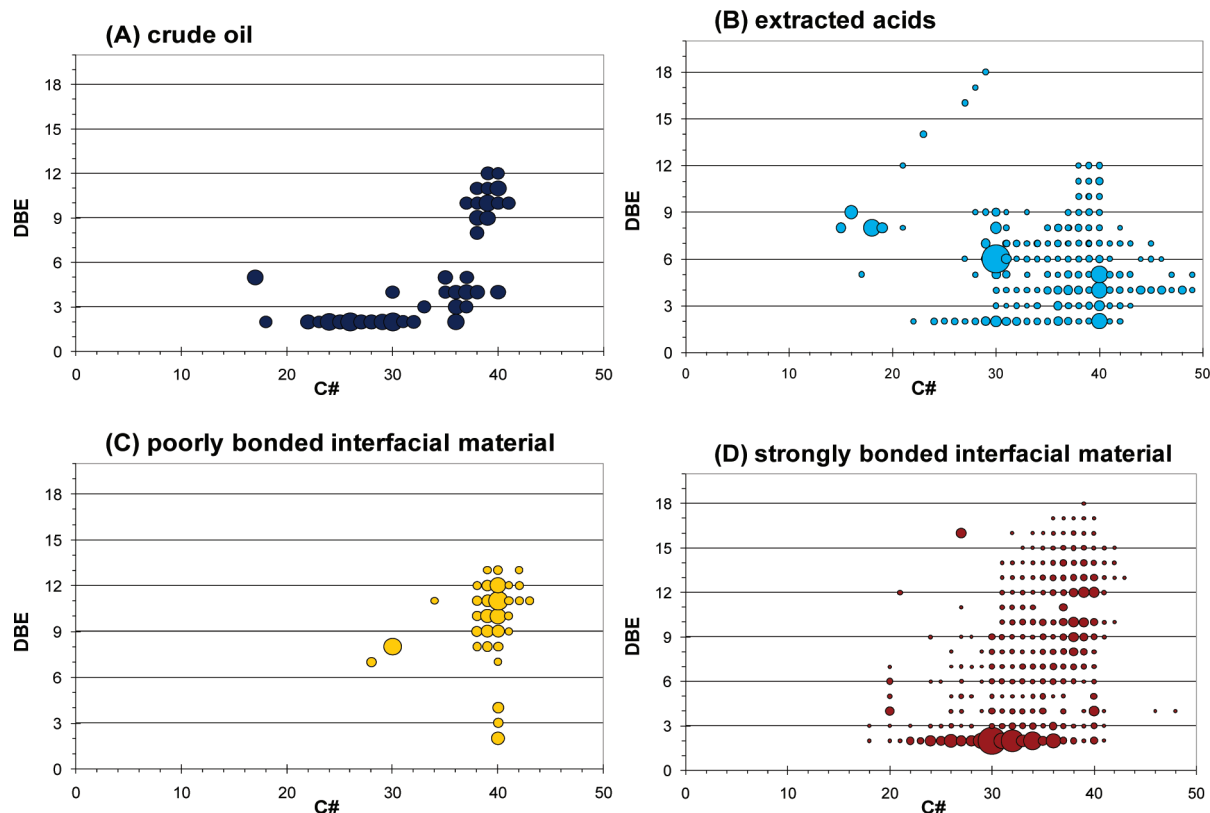


Figure 7. DBE versus carbon number plots for all species that contain four oxygen atoms per molecule (O_4 species) in the (A) crude oil (upper left), (B) acid extract (upper right), and for the (C) poorly bonded interfacial material (lower left) and (D) strongly bonded interfacial material (lower right).

aromatic rings in their structure. The eluted interfacial material, therefore, must contain fatty acids (DBE value = 1), naphthenic acids (DBE values > 1), and aromatic carboxylic acids (DBE values that are higher than possible for naphthenic structures at a given carbon number). The strongly bonded material contains almost exclusively saturated (fatty) acids with a DBE value of 1 (Figure 7D). A clear distinction between strongly bonded (fatty) acids and toluene-soluble, naphthenic and even aromatic monoprotic carboxylic acids can be made. The observed affinities of the monoprotic acids to the water–oil interface seem to be consistent with the hydrophilic properties of both acid groups.

Tetra-oxygen (O_4) Species. A small number of tetra-oxygen-containing species have been identified in the crude oil shown in Figure 7A. A higher number of O_4 species than in the oil could be found among the extracted acids as shown in the corresponding graphs (parts A and B of Figure 7), which is likely due to their enrichment by the acid extraction step. Only a small number of signals with low intensity are found in the poorly bonded interfacial material in Figure 7C. The spectrum of the strongly bonded interfacial material (Figure 7D), however, shows the largest number of O_4 species with the widest range of DBE values from 2 to 18 and carbon numbers from 18 to 42.

A highly abundant series of data points at DBE value 2 is likely to correspond to a series of aliphatic acids that contain two carboxylic acid functions per molecule (diprotic) in an otherwise saturated carbon chain. Because each carboxylic group in a molecule increases its DBE value by one, it is noteworthy that no diprotic O_4 species with a DBE value below 2 should exist in any sample and that no O_4 species with lower DBE values are observed for any fraction (parts A–D of Figure 7). The assumption of two carboxylic acid functions per molecule is also in agreement with the IR spectrum of the strongly bonded

interfacial material, where the acid functions, such as diprotic O_4 species, were found to be largely enriched. Another indication of their higher polarity is the fact that, in contrast to the O_2 species shown in the graphs in parts A–D of Figure 6, O_4 species are highly enriched in the strongly bonded interfacial material regardless of their DBE value (Figure 7D). The higher affinity of the highly unsaturated O_4 species to the interface can be explained by their stronger hydrophilic character, resulting from two carboxylic functions per molecule. The diprotic acids are attached to the water phase regardless of the carbon skeleton of the molecule. The IR spectrum of the strongly bonded interfacial material shown in Figure 3D and the mass data in the plot in Figure 7D suggest three diprotic acid types: (a) fatty (DBE value = 2), (b) naphthenic (DBE values > 2), and (c) benzoic (DBE values higher than can be explained by naphthenic rings at the given carbon number).

Asphaltenes. The mass spectral data obtained for the asphaltenes contain a significant number of oxygen sulfur species. Obtaining a mass spectrum of the asphaltenes was complicated by the high level of sodium chloride in the sample. The latter salt is not considered a “proper” asphaltene but results probably as a co-soluble species entrained in the form of micro-water droplets in the pentane precipitate. Figure 8 shows mass spectrometric data for the oxygen sulfur species (O_3S and O_2S in the upper left and right graphs, respectively) and for oxygen species (O_2 and O_4 in the lower left and right graphs, respectively). The alkyl benzene sulfonates (O_3S) with a DBE value of 4 and 17–19 carbon atoms found in the oil and the strongly bonded interfacial material are also found in the asphaltene fraction.

The DBE values and carbon numbers of O_3S and O_2S species in the poorly bonded interfacial material and asphaltene fraction show similar patterns, as displayed in Figures 4C and 5C, respectively. The slight discrepancy between the data for the

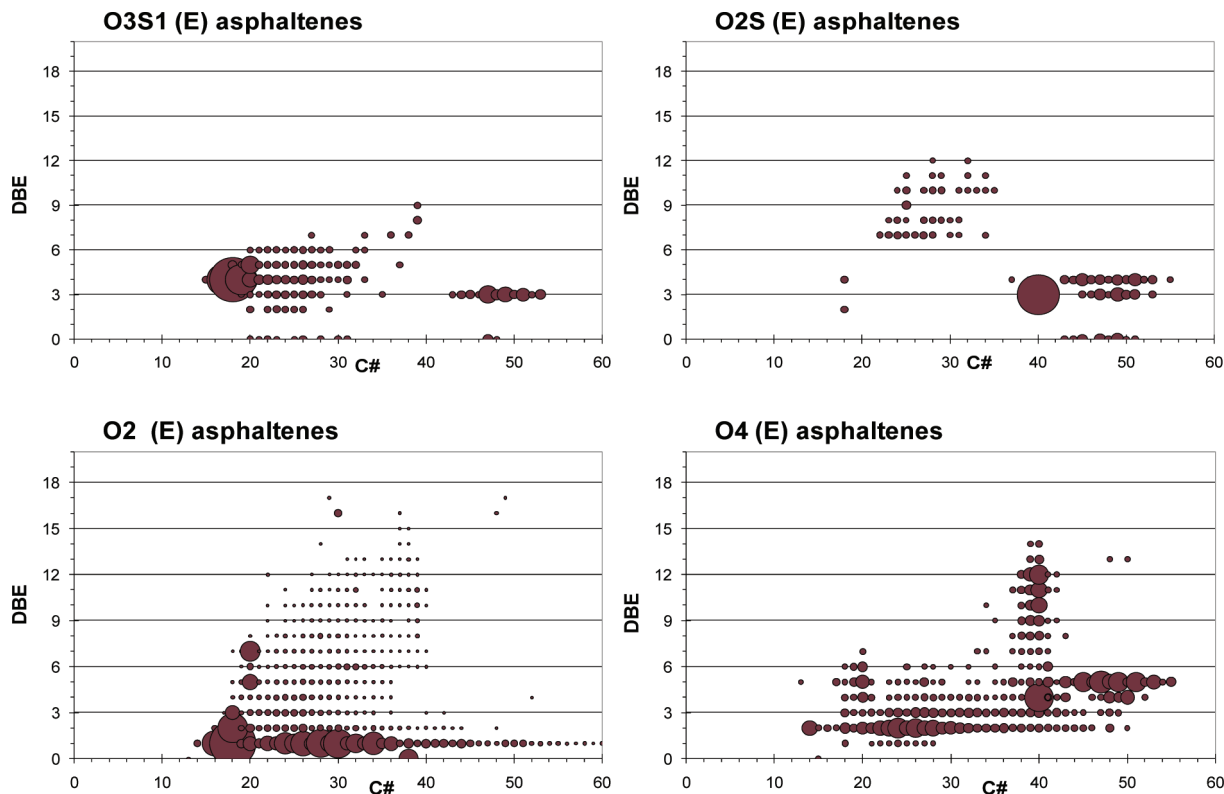


Figure 8. DBE versus carbon number plots for oxygen sulfur (O_3S) and oxygen (O_x) species in the asphaltene fraction (E). The upper left graph shows O_3S species, and the upper right graph shows O_2S species. The lower left graph displays O_2 species, and the lower right graph displays O_4 species.

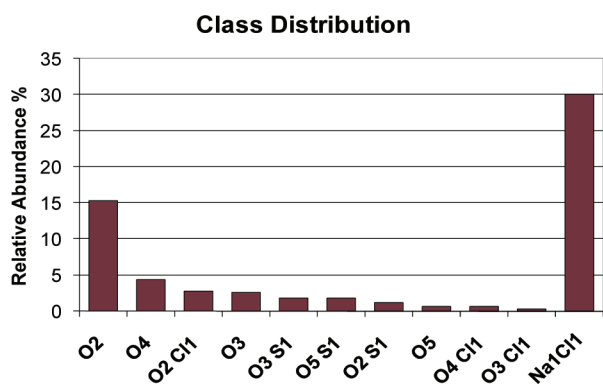


Figure 9. Class distribution of heteroatom classes measured by FT-ICR-MS in the asphaltene fraction (E).

O_2S and O_3S species, found in the asphaltenes and the poorly bonded interfacial material, may be attributed to the interference from the high salt concentration in the asphaltene sample. The oxygen species identified in the asphaltenes equally resemble the carboxylic acids found in the interfacial material. The same pattern of monoprotic acids obtained for the asphaltenes (O_2 in Figure 8 on the lower left) is also found in the poorly bonded interfacial material (Figure 6C). The diprotic acids identified in the asphaltenes (O_4 in Figure 8 on the lower right) match the diprotic acids found in the strongly bonded interfacial material shown in Figure 7D in terms of carbon numbers and DBE range. The Figure 9 summarizes the findings for all classes found in the asphaltene mass spectrum.

To study the relation between poorly bonded interfacial material and asphaltenes further, asphaltenes in the poorly bonded interfacial material and oil were determined by pentane precipitation. The poorly bonded interfacial material yielded 24 wt % asphaltenes versus the 5–8 wt % asphaltenes that were obtained from the crude oil. The asphaltene content in the

weakly bonded interfacial material is, therefore, significantly higher than the asphaltene content of the supernatant oil.

Discussion

Species that contain one or more oxygen atoms are found with a higher abundance in the strongly and poorly bonded interfacial material, more so than in the crude oil. Figure 10 presents the relative abundance of the different compositional classes identified in the oil (A) and the separated fractions (B–D). Compound classes are labeled with reference to the type and number of heteroatoms ($N_xO_yS_z$). The abundances were summed from the absolute abundance of all signals for each class and normalized over all identified signals in the corresponding mass spectrum. The di-oxygen (O_2) class is the most abundant class in the interfacial material, with relative abundances comparable to the one observed for the extracted acid sample. This enrichment of O_2 species in the acid extract, in combination with the observation of carboxylic acid groups by IR spectroscopy, points toward monoprotic carboxylic acids as a functional feature for the O_2 class. The O_1 class is largely found in the poorly bonded interfacial material and was, as expected, not extracted into the acid fraction. The O_3 class is present in the extracted acid fraction and in both interfacial materials (C and D). The O_4 species are present with a higher abundance in the mass spectra for the strongly bonded interfacial material (D) than in one of the extracted acids (B), but it is present with a lower abundance in the poorly bonded interfacial material (C). The O_4 class is, therefore, strongly enriched at the interface and likely corresponds to diprotic carboxylic acids as indicated by the corresponding IR spectrum (Figure 3D).

Oxygen–sulfur-containing species exist in the crude oil (A) in low numbers and with low abundance and are negligible among the extracted acids, but they are found in higher numbers

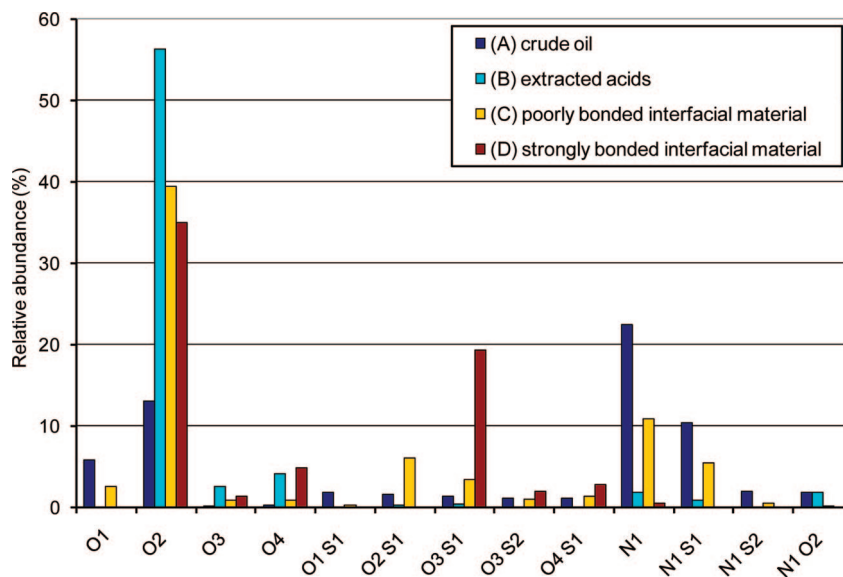


Figure 10. Comparison of the relative abundances of the main classes identified by FT-ICR-MS in (A) the crude oil, (B) the extracted acids, (C) the poorly bonded interfacial material, and (D) the strongly bonded interfacial material.

Table 1. Summary of Identified Species at the Water–Oil Interface

interface structure	monoprotic carboxylic acids	diprotic carboxylic acids	S ₁ O ₃	S ₁ O ₂	nitrogen species ^a
primary, strongly bonded material	fatty	all structures	acidic and non-acidic		
secondary, weakly bonded material	naphthenic and aromatic		non-acidic	non-acidic	

^a Nitrogen species were negligible in the interfacial material.

and significantly higher intensities in the interfacial material fractions (C and D). This distribution of O_xS species reveals their selective adsorption at the water–oil interface. O₂S species are mostly present in the poorly bonded interfacial material (C), whereas O₃S species seem distributed between the eluted and the strongly bonded interfacial material, with a greater abundance in the latter. A comparison of the previously discussed classes in the oil (Figure 10) and the asphaltenes (Figure 9) shows the following differences: The asphaltenes contain comparably higher levels of O₄ species (diprotic acids) than the crude oil. O_xS species were also identified in significant amounts in the asphaltene fraction, indicating the contribution of asphaltene material to the emulsion stabilization. Predictably, the asphaltene content in the poorly bonded interfacial material was significantly higher than in the crude oil with 24 wt % asphaltenes in the interfacial material, compared to 5–8 wt % obtained for the oil. These results are comparable to those obtained in a previous study on water bitumen interfaces by FT-ICR-MS that showed selective adsorption of oxygen and oxygen–sulfur species in the interfacial material.^{5,9}

Nitrogen, nitrogen–oxygen, and nitrogen–sulfur species are present in the oil to a low extent. Although nitrogen species were not the main focus of this study and their ionization by the used ionization mode (ESI negative) is poor, some nitrogen species could be seen. In particular, some nitrogen di-oxygen species are extracted into the acid fraction, indicating nitrogen-containing carboxylic acids. Nitrogen species are, however, found with a lower abundance in the poorly bonded interfacial material than in the crude oil. No nitrogen-containing species were identified in the strongly bonded interfacial material, revealing their poor adsorption at the water–oil interface. Their detection in the poorly bonded interfacial material could probably be attributed to oil entrapped in the emulsion. Nitrogen

species are classically considered as constituents of asphaltenes²⁶ but were not identified in significant numbers and quantities in the poorly or strongly bonded interfacial material of this oil, despite the resemblance of these fractions to asphaltenes. The asphaltene fraction of this oil should, therefore, be understood in terms of heteroatom classes to reflect its heterogeneous affinity to the oil–water interface. Oxygen- and oxygen–sulfur-containing asphaltene species are clearly associated with the oil–water interface, while nitrogen-containing species seem to be of lesser importance for the stable emulsions exhibited by this particular oil.

Conclusion

The interfacial material can be divided into two groups of compounds that contribute to the emulsion stability as shown in Table 1. A primary group of oil components that are strongly bonded to the water–oil interface stabilizes the emulsion even after repeated washing with toluene. This primary group consists of (a) saturated (fatty) monoprotic acids, (b) saturated, naphthenic, and aromatic diprotic acids, (c) alkyl benzene sulfonates (sulfur tri-oxygen-containing compounds), which may be an oil additive, and (d) sodium chloride salt from the formation water.

A secondary group of components that is more loosely attached to the interface contributes to the emulsion stability but can be removed by repeated washing with toluene. This second group consists (a) of naphthenic and aromatic monoprotic acids and (b) non-acidic sulfur tri-oxygen- and sulfur di-oxygen-containing compounds. The poorly bonded interfacial material shows a significant similarity to the asphaltene fraction in their

(26) Roussis, S. G.; Fedora, J. W.; Fitzgerald, W. P.; Cameron, A. S.; Proulx, R. Advanced molecular characterization by mass spectrometry: Applications for petroleum and petrochemicals. *Analytical Advances for Hydrocarbon Research*; Hsu, C. S., Ed.; Kluwer Academic: New York, 2003; Chapter 12, pp 285–311.

IR spectrometric signatures and in terms of the identified species. This observation is in agreement with the high asphaltene content of the poorly bonded interfacial material. Nitrogen-containing molecules that are traditionally also regarded as asphaltene or resin components²⁶ were identified at lower levels in the interfacial material than in the crude oil, indicating their lesser importance for the emulsion stabilization because they seem not to be enriched at the interface.

In summary, the first, strongly bonded layer of highly polar acidic species could enhance the absorption of certain,

oxygen–sulfur-containing asphaltene molecules at the interface, which in return strengthens the emulsion further.

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