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Structural Characterization and Interfacial Behavior of Acidic Compounds Extracted from a North Sea Oil

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Indigenous acidic crude oil compounds cause problems with regard to both the production and refining of crude oils. In this work, we have studied the molecular composition and interfacial properties of different acidic fractions. A North Sea acidic crude oil has been washed subsequently with pH 7, pH 10, and pH 14 aqueous solutions, resulting in three acidic fractions and three alkaline washed crude oils. The original crude oil, the acidic fractions, and the pH washed oils have been characterized by electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) and by Fourier transform infrared spectroscopy. The emulsion stability of water-in-oil emulsions of the original crude oil and the alkaline washed crude oils has been determined by the critical electric field cell method. Further, the interfacial properties of the acidic fractions and the alkaline washed oils have been examined. FT-ICR MS shows that 90% of the acidic compounds from this crude oil consist of carboxylic acids, with molecular weights in the range 300−800 Da. Removing the acidic compounds from the crude oils increases the interfacial tension and increases the water-in-oil emulsion stability, indicating that such indigenous acidic compounds destabilize water-in-oil emulsions.

Introduction

The increasing interest in naphthenic acids is due to production and processing problems of acidic crude oils. In the production step, one encounters problems with naphthenic acids in separation because of the precipitation of metal salts (usually calcium naphthenates)[1−4] and problems with the produced water quality because of dissolved acids.[5] More recently, Baugh and co-workers[6] also demonstrated that naphthenic acids forming naphthenate do not necessarily resemble the majority of the naphthenic acids existing in the crude. By characterizing a deposit from the North Sea, they showed that a narrow family of 4-protic acids in the molecular weight range 1227−1235 Da is the main contributor to naphthenate deposition. Allegedly, similar observations have also been found by analyses of deposits from other fields, including the U. K. sector and West Africa. Those findings have also been confirmed by Brandal et al.[7]

Naphthenic acids or acidic fractions in crude oils are also a major concern for the oil refinery business because of corrosion problems.[8−10] However, they also represent a resource. Commercial naphthenic acids and their metal carboxylates are used as corrosion inhibitors, as dryers in paint, as preservatives in wood, and as adhesion components in tires.[11] Separation of naphthenic acids and other acidic compounds from crude oils will therefore not only improve the oil quality but is itself a valuable resource.

Although the term “naphthenic acids” originally implied that the acids contained naphthenic rings, today it comprises cyclic, acyclic, and aromatic acids in crude oils.[12] In crude oils, naphthenic acids exist as a complex mixture of compounds with broad polydispersity in molecular weight and structure.[13−18]

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Naphthenic acids are predominantly found in immature heavy crude.[12,16] Hence, they are assumed to be generated from the in-reservoir biodegradation of petroleum hydrocarbons.[19−21] Naphthenic acids can be obtained from crude oils by liquid/liquid extraction with alkaline solutions[13,17,22] or by ion exchange chromatography.[23,24] Isolated naphthenic acid fractions and other polar fractions have been examined by Fourier transform infrared spectroscopy (FT-IR),[17,25] nuclear magnetic resonance,[17,26] and mass spectrometry (MS).[17,18,27−30]

Acidic fractions are surface-active, meaning that they accumulate at interfaces between oil and water. One interesting field to study for acidic fractions is their ability to act as antiagglomerants for hydrates. Natural gas hydrates are crystalline inclusion compounds in which gas molecules are trapped inside hydrogen-bonded water cages.[31,32] The thermodynamic conditions for gas hydrate formation are high pressure and low temperature. Such conditions are very typical for deepwater operations (Gulf of Mexico, West Africa, or Brazil) or in cold-climate operations (North Sea, Alaska, or Siberia). The hazard of hydrate formation causing blockages in production lines is one of the main concerns of field development in such environments. Today, the interest is to replace the current remedies (injection of methanol or glycol[33−36]) with low-dosage hydrate inhibitors.[37−42] These inhibitors are of two types: kinetic inhibitors and antiagglomerants. Kinetic inhibitors inhibit hydrate formation for a long period by extending the period from the beginning when the system falls into the hydrate-forming region until the onset of hydrate formation. Antiagglomerants on the other hand do not inhibit the hydrate formation but prevent the agglomeration of already formed hydrate crystals.[38,43] The hydrates will then be suspended in the fluid, rather than forming hydrate plugs.

There exists experimental verification that some crude oil systems can transport considerable amounts of gas hydrates without added chemical agents and without any plugging.[44−46] Hydrodynamic experiments have shown that a crude oil system can cotransport up to 20−30% water in an oil/gas system without plugging. Obviously, indigenous components in certain crude oils are capable of forming stable gas hydrate suspensions and avoiding agglomeration and plugging.

The physicochemical properties of naphthenic acids depend on their structural configuration, highlighting the importance of the characterization of isolated acidic fractions. Crude oils are complex mixtures, many of which are poorly characterized because of their compositional complexity and the large dynamic

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Table 1. Crude Oil Properties[a]

property	
density at 20 °C [g/mL]	0.884
viscosity at 20 °C [cP]	26
TAN	2.93
mol wt [Da]	242
saturates [wt %]	53.6
aromatics [wt %]	38.3
resins [wt %]	7.0
asphaltenes [wt %]	0.6
aromatic carbon [wt %]	18

[a] Data from Hemmingsen et al.[50]

concentration range. Electrospray ionization (ESI) Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS)[47] provides a means to characterize these polar compounds at a resolving power, $m/\Delta m_{50\%} > 300\,000$, and high mass accuracy (<1 ppm).[48,49] We have applied negative-ion ESI FT-ICR MS to acidic fractions and alkaline-washed oil samples from a North Sea crude oil (total acid number, TAN = 2.9). The TAN is defined as the milligrams of KOH necessary to neutralize all of the acids per gram of oil. Furthermore, the interfacial properties of the different samples and the effect of removing the acidic fraction from the crude oil on the emulsion stability of water-in-oil emulsions have been explored. This work confirms the findings from recent work[50] that the removal of acidic fractions from crude oil increases the water-in-oil emulsion stability.

Experimental Section

Sample. The crude oil was from a North Sea field, with physical properties listed in Table 1. Before sampling, the oil container was heated to 60 °C and shaken well, to homogenize the sample.

Preparation of the pH Washed Crude Oils and Acidic Fractions. The different acidic fractions were extracted from the crude oil according to the scheme shown in Figure 1. A total of 500 mL of crude oil was washed with 10 × 1 L of a 70% (v/v) ethanol aqueous solution at pH 7. The ethanol aqueous extraction solution was made by adding seven parts of ethanol to three parts of pH-adjusted (using KOH) distilled water. The aqueous phase from each wash was then extracted with 2 × 100 mL of petroleum ether (40−60°). The aqueous extracts were combined, and the ethanol was evaporated to avoid the formation of esters on acidifying the solution in the next step. The pH was then adjusted to ~1, before extraction with 2 × 100 mL of diethyl ether. The diethyl ether was then evaporated to obtain the polar fraction (pH 7 acidic fraction). A total of 100 mL of the washed crude oil was sampled for analysis (pH 7 washed oil), while the rest (400 mL) was further washed by the same procedure at pH 10. Again, 100 mL of the washed crude oil was sampled for analysis (pH 10 washed oil), and the rest (300 mL) was further washed by the same procedure at pH 14. This procedure yielded three polar fractions (pH 7, pH 10, and pH 14 acidic fractions) and three washed crude oil samples (pH 7, pH 10, and pH 14 washed oil). In addition, the pH 10 and pH 14 washed crude oils were washed two times with a 50% ethanol aqueous solution at pH 7 to remove alkaline residue.

Interfacial Tension. The interfacial tension was measured with a Sigma 70 tensiometer (KSV Instruments Ltd., Finland), by use of a du Noey ring. The instrument was calibrated relative to the surface tension of ultrapure water at 20 °C. All measurements of interfacial tension were performed at 20 °C. The interfacial tension was determined repeatedly until a stable value was reached.

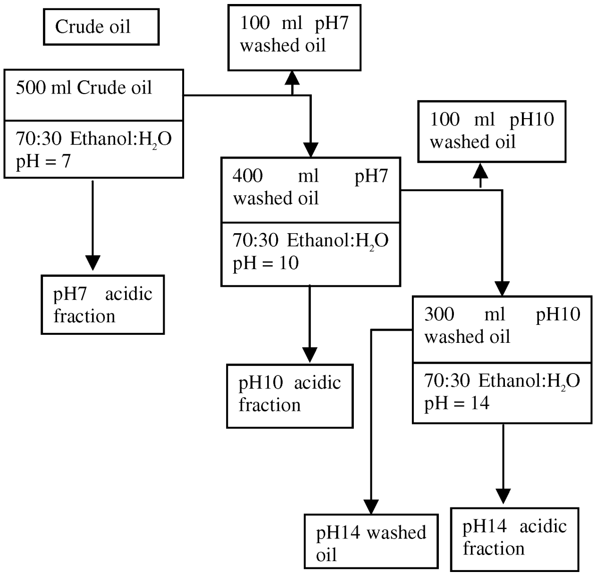

Figure 1. Extraction scheme.

Mass Analysis. Details of the procedures used for sample preparation and the conditions of the ESI FT-ICR MS analysis have been published previously.[51,52] In brief, sample solutions were prepared by dissolving oil samples at a concentration of ~1 mg/mL in a 50:50 toluene/methanol solution prior to introduction to a microelectrospray source[53] at a flow rate of 400 nL/min. A total of 1 mL of the sample solution was spiked with 4 μL of NH_4OH to ensure efficient ionization (deprotonation) for negative-ion ESI analysis: a 50 μm i.d. fused silica needle, a 2 kV needle voltage, a 300 V tube lens, and a 4 A heated capillary current were used. A home-built FT-ICR mass spectrometer equipped with a 22 cm horizontal room-temperature bore 9.4 T magnet[54] was used. Ions generated by ESI are accumulated in an external linear octopole ion trap for 20−60 s and transferred through rf-only multipoles to a 10-cm-diameter, 30-cm-long open cylindrical Penning ion trap.[55] Multipoles[56] were typically operated at 1.7 MHz at a peak-to-peak rf amplitude of 170 V. After ions were excited in the trap by broadband frequency-sweep (chirp) dipolar excitation (70−641 kHz at a sweep rate of 150 Hz/μs and peak-to-peak amplitude of 190 V), direct mode image current detection was performed to yield 4 Mword time-domain data. Time-domain data sets were coadded (200 acquisitions) and then Hanning apodized, followed by one zero fill before fast Fourier transformation and magnitude calcula-

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tion. The frequency was converted to a mass-to-charge ratio by the quadrupolar electric trapping potential approximation.[57,58] Data acquisition and processing were conducted with a MIDAS data system.[59,60] Mass spectra were externally calibrated with respect to a G241A Agilent (Palo Alto, CA) electrospray "tuning mix", and masses from the calibrated spectra were then converted to Kendrick mass and sorted according to their Kendrick mass defects.[61] Peaks were assigned by Kendrick mass defect analysis as previously reported.[52] Briefly, an elemental formula was assigned to the peak with lowest *m*/*z* value at each Kendrick mass defect. Only C, H, O, N, S, ^{13}C, and ^{34}S atoms were considered in assigning elemental formulas. The remaining peaks were assigned by adding a series of CH_2 groups to each assigned elemental formula.

FT-IR Spectroscopy of Oils and Polar Fractions. FT-IR spectra were recorded with a Bruker Optics Tensor 27 spectrophotometer, equipped either with an MCT (HgCdTe) detector and a Golden Gate diamond attenuated total reflection (ATR) cell (Specac) or with a RT-DLaTGS detector and a liquid cell. In the ATR setup, a droplet of the crude oil was placed on the ATR crystal, and the spectrum was acquired in ATR mode from 4000 to 600 cm^{-1} for 64 scans at a resolution of 1 cm^{-1}. A multivariate model was made for the prediction of TAN values in the washed oil samples. Attenuated total reflectance−Fourier transform infrared (ATR-FTIR) spectra of 27 crude oils with known TAN values (determined by potentiometric titration according to the ASTM D-664 procedure) were used in the multivariate analysis. The spectra were first-order differentiated, and a partial-least-squares (PLS) regression was performed with the ATR spectra in the range 1800−1600 cm^{-1} as input variables and TAN values in the range 0−7.5 as response variables, giving a correlation coefficient (R^2) of 0.99 with two latent variables. For a more detailed description of partial-least-squares regression, see Aske et al.,[62,63] Hannisdal et al.,[64] and Fossen et al.[65] The PLS model was constructed with Unscrambler 9.1 (CAMO).

In the liquid cell setup, the cell was equipped with KBr windows, and an optic path length of 0.2 mm was used. The spectra were recorded from 4000 to 600 cm^{-1} for 32 scans at a resolution of 4 cm^{-1}. Atmospheric compensations were performed on the spectra and, when necessary, baseline corrected. The acquisition of the spectra and the analysis were performed with OPUS 4.0 software (Bruker Optik GmbH). The amount of carboxylic acid groups in the oil samples and acidic fractions was determined by univariate calibration of the infrared spectra of stearic acid solutions of known concentrations in CCl_4. For both the calibration and determination of the amount of carboxylic acid groups, the area in the range of 1790−1624 cm^{-1} was used. The concentration of carboxylic acid groups was then converted to TAN.

Determination of Critical Electric Field. The critical electric field,[63,66,67] E_{crit}, provides a measure of water/oil emulsion stability. This technique consists of applying an increasing electric field to a stable emulsion while simultaneously monitoring the amount of current passing through the emulsion. Because of the dipolar nature of water molecules, the water droplets will align with the direction of the electric field and form chains of droplets between the two electrodes. As the applied electrical field increases, at some point, the water droplets will start to coalesce (hence, the name electrocoalescence) and a sudden increase in the current passing through the emulsion can be observed. This increase is due to a breakdown of the emulsion droplets and the formation of a continuous water channel between the electrodes. E_{crit} is defined as the electric field necessary to achieve a sudden increase in the current through the emulsion.

The cell for determining the critical field consists of a Teflon plate with a hole in the center ($r = 5$ mm) and a brass plate on each side. The distance between the plates can be varied by use of Teflon plates with different thicknesses; in this work, a thickness of 0.25 mm was used. The system is held together with isolating Teflon plates. The brass plates were connected to a computer-controlled power supply (Agilent Model 6634B) that can deliver a maximum of 100 V DC.

The crude oil samples were emulsified with 30 vol % water (containing 3.5 wt % NaCl) by use of an Ultra Turrax T18 basic rotor-stator emulsifier at 20 000 rpm for 2 min. The emulsion samples were then placed between the two brass plate electrodes, and the power supply was started at 0 V and increased by steps of 0.05 V per second.

Results and Discussion

Yield. The total yield of the acidic fractions was 1.7 wt % or 15.0 g/L of oil. Of that total yield, 58% was from the pH 7 extraction, 20% was from the pH 10 extraction, and 22% was from the pH 14 extraction.

FT-IR Spectroscopic Measurement of Oils and Polar Fractions. The amount of acidic compounds extracted from the crude oil was measured by ATR-FTIR spectroscopy. The TAN decreases rapidly during the first five extraction steps (at pH 7; see Figure 2). In addition, TAN was measured for the original crude oil and the pH washed oils (after extraction steps 10, 20, and 30) by FT-IR with a liquid cell calibrated against stearic acid solutions. There is excellent agreement between the two methods, although there is some scattering by the ATR-FTIR method, due to lower sensitivity.

A total of 12% of the carboxylic acid groups remain in the crude oil after the last extraction step. The species left in the crude oil must have very low solubility in the 70% ethanol aqueous solution, even at pH 14. Infrared spectra of the saturate, aromatic, resin, and asphaltenic fractions of the crude oil confirm that the asphaltene fraction also contains carboxylic groups, although much less than the acidic fractions. Recently published work on the same and other crude oils confirms that the asphaltenes do not extract over to the aqueous phase at pH 14 but remain in the crude oil.[50] From IR analysis of the COOH

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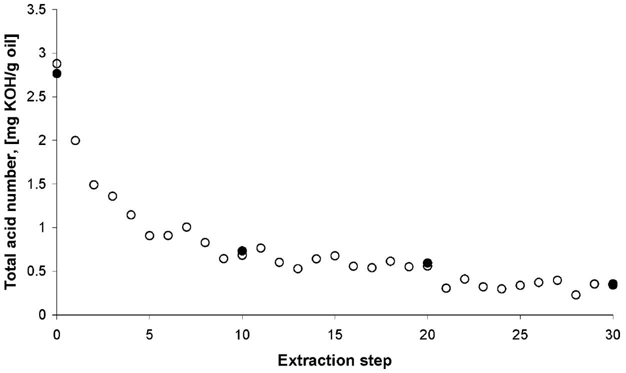

Figure 2. TAN of crude oil after each extraction step. Open circles: TAN values predicted from ATR-FTIR spectra based on the PLS regression model. Filled circles: TAN values measured with a liquid FT-IR cell calibrated with stearic acid standards. Extraction steps 1−10 are at pH 7; steps 11−20 are at pH 10, and steps 21−30 are at pH 14.

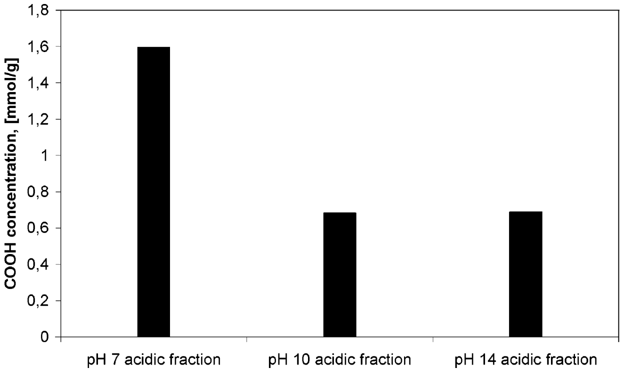

Figure 3. Concentration of carboxylic acid groups in the extracted acidic fractions.

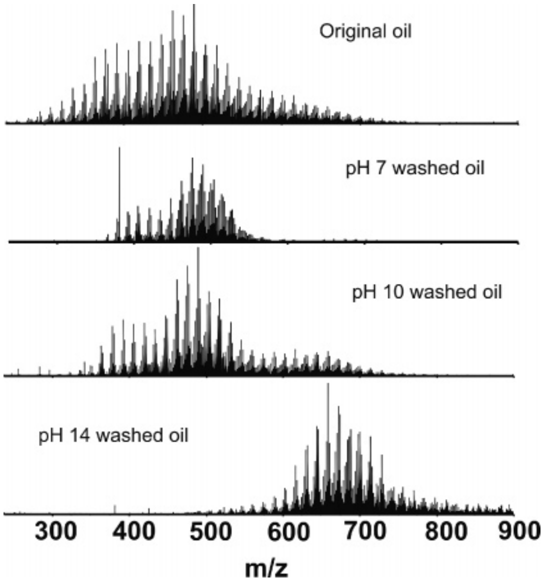

Figure 4. Broadband negative-ion ESI FT-ICR mass spectra of original and washed oil samples.

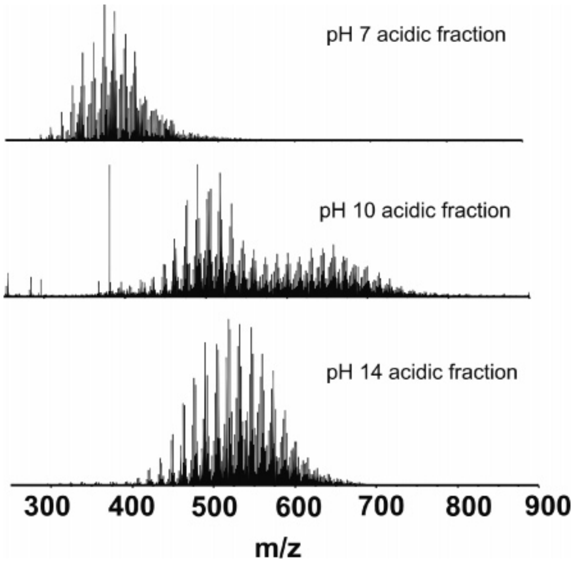

Figure 5. Broadband negative-ion ESI FT-ICR mass spectra of extracted samples.

concentration in the extracted acidic fractions (see Figure 3), the pH 7 acidic fraction contains more than twice as many COOH groups as the pH 10 and pH 14 acidic fractions, because of lower molecular weight species in the pH 7 acidic fraction. The pH 10 and pH 14 acidic fractions should also contain molecules with weaker acidic functional groups (phenols, thiophenes, etc).

Investigation of Chemical Composition by FT-ICR MS. Broadband mass spectra of washed oil and acidic fractions are displayed in Figures 4 and 5. For optimal detection of the high-mass ions, our instrument was tuned to exclude ions below *m*/*z* 300. Molecular weight distributions in each sample are clearly different, suggesting that the chemical composition can be changed by a series of extractions. For the oil samples, it is clear that the molecular weight distribution of the acidic compounds remaining in the oil increases as one extracts acidic compounds from the oil. The mass spectra confirm also the IR observation that the crude oil still contains acidic compounds even after extraction at pH 14. The mass spectrum of the pH 14 washed oil reveals that the most abundant species are distributed between *m*/*z* 600−900. At least some of these compounds should belong to the asphaltene fraction of the crude oil, thus providing an indication of the molecular weight distribution of the asphaltenes in this crude oil. Although the molecular weights of asphaltenes have been a controversial issue over the past 20 years, recent work has shown that the major fraction of the asphaltenes range from 500 to 1000 Da.[68,69]

Overall, molecules extracted by an alkaline water−ethanol mixture can be categorized roughly into low- ($m/z < 400$), middle- ($400 < m/z < 600$), and high-mass ($m/z > 600$) groups. The low-mass groups were exclusively extracted at pH 7 (Figure 5 top), as expected: smaller molecules will ultimately contain a smaller hydrophobic tail, and once the carboxylic group is dissociated, those compounds will be soluble in the 70% ethanol aqueous solution. For fatty acids and naphthenic acids, the pK_a is around 5, so that at pH 7 the carboxylic group will be deprotonated. After the pH 7 extraction, the intermediate-mass species are major ionizable components observed in the mass spectrum (refer to Figure 4, pH 7 washed oil). Spectra from both the pH 10 acidic fraction and the pH 10 washed oil have broad molecular weight distributions, mostly containing intermediate- and high-mass compounds. Washing by a pH 14 solvent resulted in a dramatic change of the mass distribution. The spectrum obtained from the pH 14 washed oil is composed exclusively of high-mass compounds: low- and intermediate-

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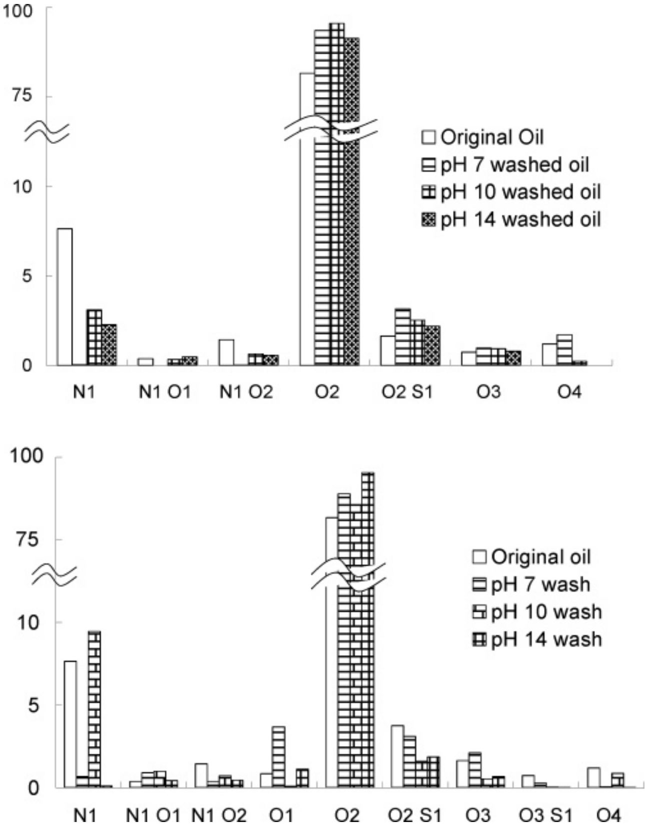

Figure 6. Distribution of heteroatom classes in oils (top) and extracts (bottom).

mass compounds are removed by the series of extractions. Interestingly, the pH 10 acidic fraction has the broadest molecular weight distribution, containing compounds with a higher molecular weight than that of the pH 14 acidic fraction.

To investigate the overall changes in chemical composition, we display distributions of heteroatom classes in Figure 6. In each figure, the abundances of dominant homologous series identified in each spectrum have been divided by the total observed ion abundance in each spectrum. The molecules in the O_2 class are dominant, accounting for 80−90% of the assigned peaks in the spectra. The O_2 groups in the compounds are believed to be composed of molecules with a “COOH” functional group. N_1 compounds are the second most abundant class in the original crude oil sample. They have been mostly extracted by the pH 10 ethanol and water mixture, indicating that N_1 species found in these spectra have a weakly alkaline character. The sensitivity for detection of each individual compound in the ESI MS analysis depends on the ionization efficiency. From our previous experience with other oil samples, carboxylic acids exhibit higher ionization efficiency than other weak acids such as phenols or thiophenes, accounting in part for the dominance of carboxylic compounds in Figure 6.

Double-bond equivalents (DBE = number of rings plus double bonds) values and carbon number distributions for the O_2 species are displayed in Figure 7. In all of the spectra, the O_2 class with DBE = 3 is the most abundant. Thus, carboxylic acids with two rings are likely the most common acidic species in this particular crude oil. The DBE distribution did not change as a result of extraction processes. However, there was a significant change in carbon number distribution among O_2 species. As shown previously in Figures 5 and 6, O_2 species in the pH 14 washed oil sample are composed of high carbon number species, leading to the higher molecular weight distribution for that sample.

Interfacial Tension. The interfacial tension of the oil against saline water (3.5 wt % NaCl) increases as acidic compounds are removed (see Figure 8). Carboxylic acids, or naphthenic acids, are interface-active, and removing them should increase the interfacial tension. The increase is highest for the pH 7 washed crude oils and levels off to a value of 24.4 mN/m for the pH 10 and pH 14 washed oils.

The interfacial properties of the acidic fractions were investigated as a function of concentration (see Figure 9). For all of the acidic fractions, the interfacial tension shows a steep decrease at low concentrations before leveling out at high concentrations. Interestingly, the pH 14 acidic fraction shows the lowest interfacial tension. To what extent different compounds lower the interfacial tension is not only dependent on the chemistry of the hydrophilic group, and size of the hydrophobic group, but also on their molecular structure and their ability to self-assemble. Also, because we have mixtures, the interactions between the different compounds in the acidic fraction may influence the final interfacial tension level.

The dynamic behavior (see Figure 10) shows that, although the interfacial tension of the pH 10 and pH 14 acidic fractions decreases rapidly and levels off at a minimum, the interfacial tension of the pH 7 acidic fraction decreases to a minimum but then starts to increase slowly with time. This behavior can be explained either by interfacial reorganization or by dissolution

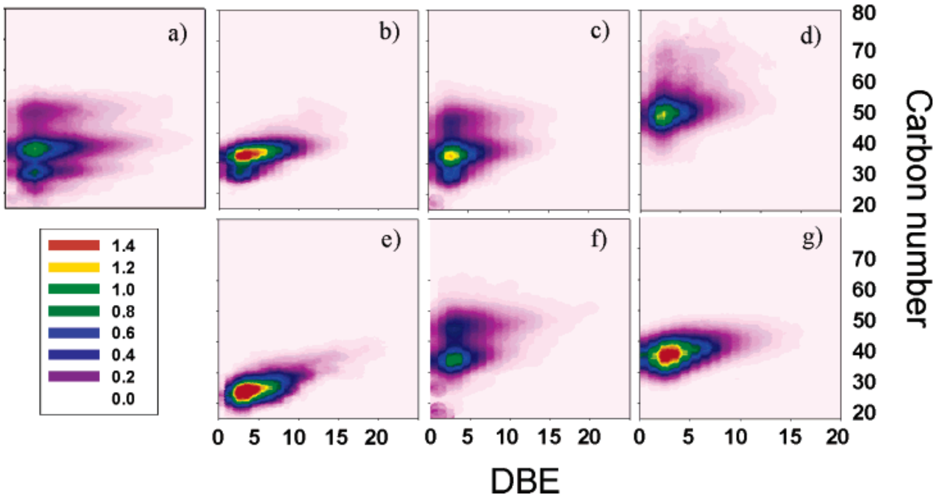

Figure 7. DBE vs carbon number distribution in (a) original oil, (b) pH 7 washed oil, (c) pH 10 washed oil, (d) pH 14 washed oil, (e) pH 7 acidic fraction, (f) pH 10 acidic fraction, and (g) pH 14 acidic fraction samples. Relative abundances are color-coded as shown.

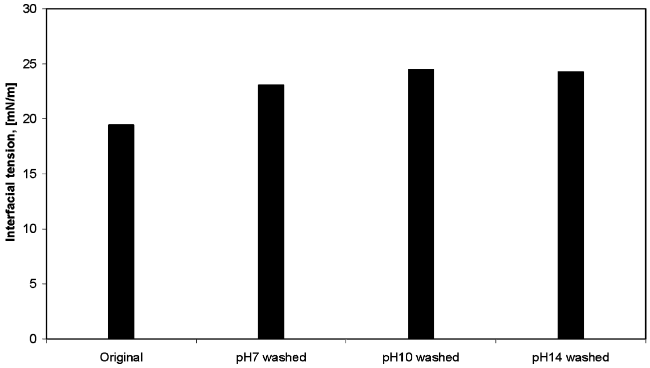

Figure 8. Interfacial tension at 20 °C for the original oil and alkaline washed oils against saline water (3.5 wt % NaCl).

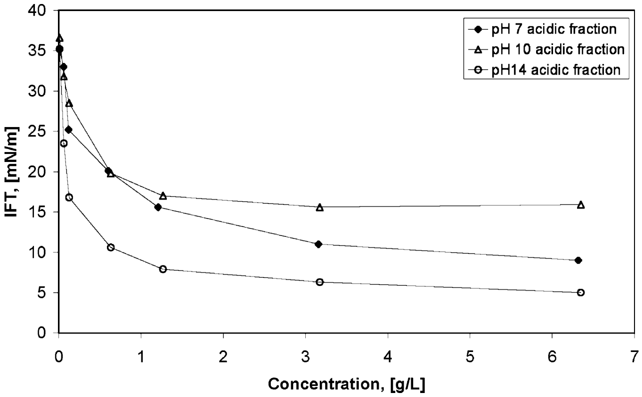

Figure 9. Interfacial tension of the acidic fractions as a function of concentration in 70% heptane/30% toluene. Aqueous phase: 3.5 wt % NaCl.

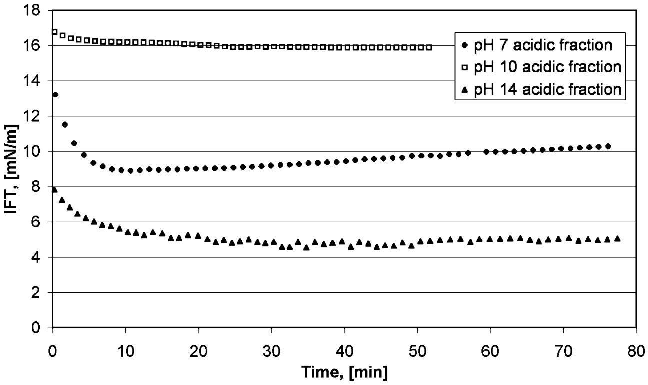

Figure 10. Interfacial tension for the acidic fractions. Concentration: 6.3 g/L in 70 vol % heptane/30 vol % toluene. Aqueous phase: 3.5 wt % NaCl.

of the interfacial compounds into the aqueous phase.[70,71] Because the pH 7 acidic fractions are extracted under neutral conditions (although with 70% ethanol), we believe that the smallest compounds in the pH 7 acidic fraction are water-soluble to a degree and that the increase of interfacial tension with time is due to the dissolution of some of these acidic compounds into the water phase.

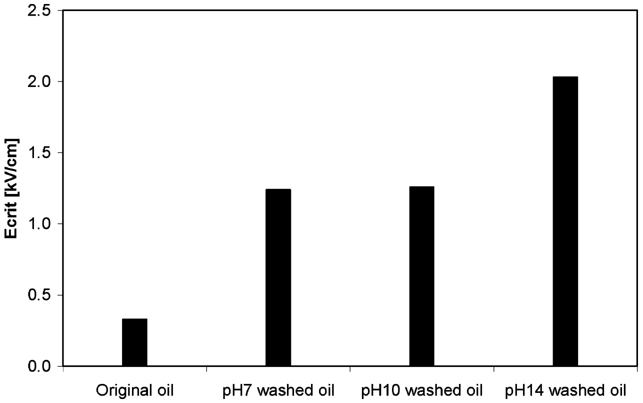

Figure 11. Water-in-oil emulsion stability measured by the E-critical technique.

As the acidic components are washed out of the crude oil, the water-in-oil emulsion stability increases (see Figure 11). There is a considerable increase in the emulsion stability after the pH 7 and pH 14 washings, whereas the emulsion stability is unaffected by the pH 10 washing. A tempting explanation derives from the interfacial behavior of the acidic fractions. The pH 7 and pH 14 acidic fractions are more interfacially active than the pH 10 fraction (according to Figure 10). As interfacially active species, they will strive for access to the water droplet interface and might either penetrate an existing interfacial asphaltenic film or prevent the buildup of an asphaltenic film by populating the water/oil interface first. Their diffusion coefficients and thereby their mobilities should be much larger than for the asphaltenes, at least for the pH 7 acidic fraction. Another explanation for the increased emulsion stability on removal of acidic compounds is that naphthenic acids interact with asphaltenes and thereby solubilize them, as shown by recent studies of the interactions between asphaltenes and naphthenic acids.[72−74] The removal of such compounds decreases the asphaltenes' solubility, resulting in larger asphaltene aggregates, more prone to forming interfacial stable films, preventing coalescence of the water droplets, as shown by the critical electric field cell method (E-critical) measurements. Both of these effects, the high interfacial activity by the acidic fractions and the solubilizing effect on asphaltenes, can explain the increase in emulsion stability on removal of the acidic compounds from the crude oil.

Conclusions

Water-in-oil emulsions become more stable as indigenous acidic compounds in a North Sea crude oil are removed by extraction, indicating that such indigenous compounds play an important role in the destabilization of water droplets. Acidic compounds are surface-active and may hinder asphaltenes and other resins from forming stable films around the droplets. Acidic compounds are also known to have a solubilizing effect on asphaltenes, and removing them from a crude oil may cause the asphaltene to aggregate more easily at the water/oil interface.

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ESI FT-ICR MS shows that 90% of the acidic compounds from this crude oil consist of carboxylic acids, with molecular weights in the range 300−800 Da. Most of the acidic compounds are removed during an initial extraction at pH 7. However, ∼12% of the total acids in the crude oil still remain in the crude oil, even after extraction at pH 14. ESI FT-ICR MS shows that the remaining acidic compounds have molecular weights above 600 Da, and we can conclude that these species have very low solubility in the 70% ethanolic aqueous phase.

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