Dynamics of Molecules Observed at Crude-Oil−Gas Interfaces by Time-of-Flight Secondary Ion Mass Spectrometry Imaging

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ABSTRACT: Time-of-flight secondary ion mass spectrometry (TOF-SIMS) imaging provides molecular speciation at the micrometer scale, while the penetration depth of the primary ion beam is limited to the top-layers of a sample. These combined properties make TOF-SIMS potentially an ideal technique to study oil−gas interfaces. TOF-SIMS spectra of three crude oils were evaluated, and only low-mass fragment ions could be assigned to molecular structures unambiguously. Films of crude oils were incubated under air, oil vapor, or water vapor for various times. TOF-SIMS images of a polar crude oil revealed feeble structures of ∼10 μm large round patches that grew to ∼30 μm large crystals when incubated under air and oil vapor, respectively. Principal component analysis of the images showed that the continuous phase had typical aromatic signatures, while the patches and crystals had alkane-like characteristics. No features showed up when the oil film was incubated under water vapor, which indicated that saturated water vapor prevented the accumulation of nonpolar alkane-like compounds at the oil−gas interface. These examples showed that crude oils do not behave as dead fluids but that their constituents accumulate at the oil−gas interfaces in a dynamic way.

KEYWORDS: crude oil, TOF-SIMS imaging, TOF-SIMS spectra, surface microstructure, image analysis by principal component analysis

INTRODUCTION

The growth of both the world population and wealth have steadily driven an increasing demand of energy, which is presently primarily obtained from fossil fuels. After decades of exploration, easily extractable light oils have become depleted and the oil industry has been forced to switch to heavier oil grades that are more complex and more difficult to handle.1 The extraction and processing of heavy oils are more prone to the formation of deposits that plug the pores in the permeable reservoir, obstruct oil pipelines, or cause other fouling problems. The high costs associated with these challenges related to instable oils justify detailed analyses of crude oil chemistry. Crude oils are among the most complex molecular mixtures,3,4 and with a wide range of analytical techniques, a plethora of molecules can be identified that make up their composition. The volatile fraction can be identified by high-resolution two-dimensional gas chromatography (GC×GC).5,6 Often, n-alkanes dominate the composition, but at lower concentrations, there are numerous homologous series of branched, cyclic, aromatic, and relatively polar heteroatom bearing molecules. Due to the underlying molecular complexity, each oil sample is a unique molecular ensemble that reacts differently.

It is a challenge for the petrochemist to associate chemical and physical properties of crude oils with a proper analysis of the underlying complex molecular composition. At a high level, elemental analysis shows that oils are composed primarily of carbon (C) and hydrogen (H) with small amounts of the heteroatoms, specifically sulfur, oxygen, and nitrogen, which make up various relatively polar and more reactive functional groups. Generally, both the heteroatom content and the aromaticity increase with heavier oil types.6 The impact of heteroatoms on the molecular complexity is vast because they increase the number of elemental combinations exponentially. One way to characterize oils is by SARA-analysis according to IP-143, where the oil is separated in the four solubility fractions: saturates, aromatics, resins and asphaltenes (SARA). Saturates and aromatics are fractions of almost pure hydrocarbons and usually make up the bulk of the oil composition. Both resins and asphaltenes are relatively rich in heteroatoms. Resins are the
class of polar molecules that are still soluble in alkanes, while asphaltenes are defined as the class of substances that is insoluble in alkanes such as heptane but that is soluble in aromatic solvents such as toluene.1 In general, asphaltenes make up the most complex fraction.8 Compared to resins, asphaltenes are more aromatic and their average molecular weight of ~750 Da is higher.7,9

In native crude oil, thousands of different chemical substances interact with each other according to the “like-dissolves-like” principle.10,11 As long as the solubility parameters of individual classes match sufficiently, the hydrocarbon mixtures form one single liquid phase that appears homogeneous at the macroscopic scale. However, there are plenty of examples of nonstable oils, whence solid materials can precipitate during the extraction and processing of the liquid. Notorious organic deposits include asphaltenes, diamondoids, and high molecular weight paraffins and waxes, especially when they are present in high concentrations.

Phase separation of deposits often starts at interfaces where the oil comes in contact with another media, like gas bubbles, water, brine, or solid surfaces of minerals (reservoir rock) or metals (pipelines). Accumulation of specific classes of molecules at interfaces increase their concentration locally. For example, the most interface active asphaltene species make up less than 2% of the whole asphaltenes fraction,12 and analysis of interface materials that were isolated from oil–water interfaces revealed enrichment of polar O2− and O−, as well as N2µ, and N2Oµ species compared to the composition of the parent oil.13−15. The adsorption of the relatively low molecular weight resins is in competition with the adsorption of asphaltenes at the oil–water interfaces.16 Hence, it can be concluded that the composition of interface layers can be quite different from that of the bulk of the oil and, second, that the molecular composition of interface layers can be dynamic in time.

In this paper, we employ time-of-flight-secondary ion mass spectrometry (TOF-SIMS) to study crude oils and explore the capability of TOF-SIMS imaging to study molecular speciation at interfaces of native crude oils. Understanding of the chemistry at oil interfaces is of importance because potential fouling problems often start there. Oil films served as simple models for oil–gas interfaces, and it was found that the composition of the interface layer depends on the gas composition. Principal component analysis was applied to visualize and analyze the chemical speciation in TOF-SIMS images.

**EXPERIMENTAL SECTION**

Three crude oil samples with different characteristics were provided for testing by Shell Global Solutions International B.V. One sample was a blend of crude oils that easily emulsifies (no further data given), the second was a hydrophobic crude with API 41.6 and a viscosity of 3.3 mPa·s, and the third was a very polar oil with API 25.5 and a viscosity of 22 mPa·s.

An oil droplet was spread out with a cover glass on indium–tin oxide coated glass objects. The film was left to dry at the air or underneath a glass bell for 1 to 120 min. The sample was put in a desiccator at pressure of ~10−2 bar for 30 min after the incubation. The sample was subsequently transferred into the vacuum lock of the TOF-SIMS where it was left under high vacuum (~1.3 × 10−7 bar) for 1 h in order to get rid of the most volatile molecules. Next, the sample was transferred for analysis into the measurement chamber of a triple-focusing (TRIFT) II system TOF-SIMS (Physical Electronics, Chanhassen, MN). A 22 keV primary gold-ion beam of 600 pA hit the sample at an angle of 45° with pulses of 19 ns. Mass spectrometric images with tile sizes of 150 × 150 or 200 × 200 µm were projected on a 256 × 256 pixel-detector. This corresponded to squared pixel sizes of ~0.6 and ~0.8 µm, respectively. For a tile size of 150 × 150 µm, about half of the static limit of 103 primary ions per square centimeter was reached after 23 min of acquisition time. The raw data were recorded with WinCadence 4.7.1.

The raw TOF-SIMS image data were converted to a matlab format with our in-house ChemomeTricks software, using a bin size for mass channels of 0.1 Da and peakpick parameters n1 = 1, n2 = 50, and threshold = 1. The images of the converted data were analyzed by PCA (trifttricks V1.54).

For GC×GC, residues were dissolved in cyclohexane and analyzed on an Agilent 7890 GC equipped with a DB-1 column (100% methyl) in the first dimension and a ZOEX thermal modulator and a DB-17 column (50% phenyl/50% methyl) in the second dimension. A JEOL AccuTOF MS (resolution 6000) was used for mass analysis and detection.

**RESULTS AND DISCUSSION**

**Sample Preparation.** The first challenge for TOF-SIMS analysis was to prepare crude oil samples and to introduce them into the vacuum of a mass spectrometer. The aim was to retain the natural molecular interactions as much as possible, and therefore, nondiluted native crude oil was used in all experiments. An oil droplet was spread out over a target with a glass bar in order to create a fresh oil surface. In the simplest setup, the oil film was exposed to air, creating an oil–air interface. An incubation time of minutes to hours was employed, during which oil molecules could rearrange at the new oil–air interface. As a side effect of this treatment, the most volatile fraction evaporated during the incubation process, and it was observed that the viscosity of the film residue increased after prolonged incubation times.

A sample will undergo much more severe loss of volatiles when being transferred into the high vacuum of a TOF-SIMS for analysis. Consequently, a rapid increase of the viscosity slows down the molecular diffusion through the film. As a part of the sample prep method, the incubation was quenched by placing the film sample into a vacuum chamber in order to rapidly fix the spatial position of the molecules. The actual loss of volatiles under a vacuum was measured by GC×GC−MS.

Figure 1 shows the GC×GC−MS chromatograms of the polar oil and its residues after exposure to high-vacuum conditions (<1.3 × 10−7 bar) for 1 h and overnight. The peak heights are color coded from black/blue for the baseline background to red for the most abundant peaks. Compounds are separated by their boiling point (bp) in the first dimension along the x-axis of the figure, with increasing bp values from left to right. Clearly, after 1 h, all volatiles with a boiling point below that of n-octadecane (nC18, bp 316 °C) were stripped. Its molecular mass of 226 Da indicates the absolute lower limit of molecular ions detected by TOF-SIMS analysis. Overnight exposure topped off everything below tetracosane (nC24), which has a boiling point of 391 °C and a molecular mass of 338 Da. Combined with a simulated distillation analysis, data that unfortunately was not available, it would be possible to estimate the percentage of material that was lost from the oil film. Once the sample was stripped from volatiles, TOF-SIMS measurements were straightforward.

**Evaluation of TOF-SIMS Imaging.** TOF-SIMS imaging is an established analytical technique that allows for the study of samples without the need of preselection or labeling of the analytes.19−21 Analytes were both desorbed and ionized by a
Figure 1. Total ion current GC×GC chromatograms of polar oil and the loss of its volatiles after 1 h and overnight residence time in the vacuum lock of the TOF-SIMS machine. The first GC-dimension is plotted on the x-axis and represents a boiling point separation with increasing boiling points to the right; the second separation is based on polarity and is plotted on the y-axis with nonpolar alkanes at the bottom.

Figure 2. TOF-SIMS spectra of three distinct crude oil types.

The literature of TOF-SIMS of crude oils is sparse. Previous studies reported measurements of biomarker standards and their detection in petroleum inclusions.\textsuperscript{19,23−28} Primary and secondary petroleum fluid inclusions could be distinguished by TOF-SIMS.\textsuperscript{20} Recent studies detected aliphatic wax structures against aromatic background in TOF-SIMS images of bitumen surfaces.\textsuperscript{20,25} and probed molecular structures of asphaltenes in terms of aromaticity and alkyl content.\textsuperscript{22} Most important, the fragmentation observed by TOF-SIMS strongly resembles that of electron ionization spectra,\textsuperscript{19} which implies that fragment ions can be interpreted by established electron impact reaction mechanisms.\textsuperscript{31}

Figure 2 shows the positive ion mode TOF-SIMS spectra of three distinct crude oils that were described as a blend that easily emulsifies, as a hydrophobic and a very polar oil. These spectra present the accumulated signal from 65 536 pixels, which each act as individual detectors. The high-energetic ionization character became apparent from the high abundance of low molecular weight fragment ions below the 226 Da limit that was found by GC×GC analysis. The most abundant ions corresponded to generic alkyl-fragment ion series \( m/z 15, 29, 43, 57, 71, 85, 99, 113, \text{ etc.} \) and cycloalkyl- or alkenyl-fragment series \( m/z 27, 41, 55, 69, 83, 97, \text{ etc.} \)\textsuperscript{31} Any alkenyl ion should have been formed \textit{in situ} because olefins are usually not present in crude oils.\textsuperscript{3} The low end of the spectra showed surprising little differences despite the fact that the oils had very different characters. This result indicates that their TOF-SIMS fingerprints reflect bulk properties that are characterized dominantly by alkane fragments, and no large mass peaks of any heteroatom bearing fragments were observed.

Larger fragment ions and (pseudo) molecular ions that contain more specific molecular information showed up in the medium and high-mass ranges between \( m/z 200 \) and 1000. In Figure 2, these signal intensities were multiplied for visualization and reveal distinct patterns in the high molecular weight tails that differentiate the oils. The hump around \( m/z 400 \) in the spectrum of the polar oil corresponds to (pseudo)molecular ions of the hopanes that were abundant in the GC×GC chromatogram in Figure 1. TOF-SIMS of biomarker standards of cholesterol and hopane\textsuperscript{25} showed deprotonated molecular ions \([M - H]^-\), while we just observed protonated molecular ions \([M + H]^+\) for a paraffin standard that was mixed with the polar oil in a ratio of 2:1. The occurrence of multiple (chemical) ionization channels complicates the interpretation of the mass peaks in the medium and high-mass regions and stresses the need for standard compounds to verify mass assignments. In addition, the probability that any heteroatoms were included increases with the mass of the ions. Although different ionization methods were applied, crude oil studies with very high-mass resolution Fourier transform MS revealed complex isobaric peak patterns of ions with various elemental compositions within each nominal mass unit.\textsuperscript{1,8} The present analytical record is the measurement of 244 779 unique elemental compositions across
the mass range \( m/z \) 260−1505 with a mass resolving power of \( \sim 3 \) million fwhm.\(^3\) Deconvolution of isobaric patterns requires high-mass resolutions (>100 000), something that cannot be achieved by the present TOF-SIMS instruments, which are limited to mass resolutions of 5000−10 000.\(^1\),\(^2\),\(^3\) The lack of mass resolution together with uncertainties about the ionization channels hamper any unambiguous assignments of (nominal) mass peaks in TOF-SIMS spectra to specific oil compounds in the mass range above the 226 Da limit found by GC×GC analysis.

Figure 3A shows the principal component analysis (PCA)\(^2\) score plot image of a 200 × 200 μm large area from an "air-dried" film of the polar oil that was incubated for 35 min. Although the first principal component (PC1) function described only 0.38% of the total variance and had a small eigenvalue of 2.2, it clearly showed structural features of round island structures of \( \sim 10 \) μm in diameter. The formation of the island structures turned out to be very reproducible when the film was dried to the air for 5−35 min. A featureless image was obtained at shorter incubation times, which indicated that some time was required for the formation of the islands. Featureless, homogeneous images were also recorded for the two other crude oils, independent of the applied incubation time. The absence of features, however, does not exclude their presence since the lateral resolution in these experiments was in the (sub)micrometer range and structures smaller than this size would escape detection.

Figure 3A also shows the loading plot of PC1, which correlated in the PC1+ direction with the island structures and in PC1− with the continuous phase. The loadings of high masses \( m/z \) > 600 contained no relevant signal and were omitted for the reported PCA calculations. All the PC1+ peaks are associated with saturated alkane elements, such as the alkyl-chain fragment ions \( m/z \) 15, 29, 43, 57, 71, 85, 99, 113, etc. and the cycloalkyl-fragment series \( m/z \) 27, 41, 55, 69, 83, 97, etc.\(^3\) Therefore, the islands are concluded to bear an alkane-like signature.

The peaks in PC1− are associated with aromatic structures, such as the phenyl cation \( (m/z \) 77), and alkyl-substituted homologous of the tropylium ion or benzyl cation \( (m/z \) 91, 105, 119, etc.), indene cations \( (m/z \) 115, 129, 143, 157, etc.), and benzotropylum ions \( (m/z \) 141, 155, 169, 183, etc.). Similar aromatic mass peaks were observed in TOF-SIMS spectra of isolated asphaltenes.\(^2\) As suggested by Sjövall et al., the even mass peaks \( m/z \) 128 and 178 could represent radical cations of naphthalene and phenanthrene or anthracene, respectively, but these mass peaks have to be fragments from larger structures since the GC×GC data in Figure 1 showed that the sample was

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Figure 3. (A) 200 × 200 μm TOF-SIMS image of a film that was air-dried for 35 min. The loading plot shows aliphatic characteristics in PC1+ for the red area and aromatic characteristics in PC1− for the green/blue area. (B) 150 × 150 μm TOF-SIMS image of a film that was incubated underneath a glass bell for 150 min.
devoid of compounds with a molecular weight of <226 Da. From m/z 115 toward higher masses, the PCA loading seemed to develop as a continuum of (alkyl-substituted) aromatic structures. It was concluded that the PCA images assigned alkane-like fragments to the island structures and aromatic structures to the continuous phase.

**Influence of the Atmosphere Composition.** Encouraged by the unexpected results, the sample preparation method was further optimized. A small glass bell was placed over the film in order to reduce the evaporation of volatiles and to extend the incubation time under more constant conditions. The top of the bell was filled with a small aliquot of the same oil in order to assist the saturation of the vapor of the most volatile fraction.

Figure 3B shows a 150 × 150 μm PCA image and PC1 loading plot of a film that was incubated underneath the bell. In this example, the PCA described 1.3% of the variance by PC1 and resulted in an eigenvalue of 10.5, compared to 0.38% and an eigenvalue of 2.2 of the previous experiment. This result indicated that the contrast between the features and the continuous phase was significantly enhanced by the prolonged incubation underneath the glass bell. The most striking feature in the image was that crystal shapes instead of round patches were formed against a continuous background. It should be noted that the broad black boundary zones are artifacts of the PCA contrast enhancement procedure; these black areas are groups of pixels with small loading factors in PC1 or PC1+.

The diameter of the largest crystals was ~30 μm, which was significantly bigger than the ~10 μm large round patches in Figure 3A.

The PC1 loadings plot in Figure 3B reproduced the mass peak patterns in Figure 3A, and in addition, the high-mass region of the spectrum contained information up to m/z 1000. The loading plot of the crystals showed a strong aliphatic signature in the low-mass region combined with a continuous series of unidentified peaks above m/z 650. The latter indicated that the crystals contain high molecular weight substances. A reference experiment with a ~460 Da paraffin standard showed a major ion series of protonated paraffin molecules (C\(_n\)H\(_{2n+2}\)·H\(^+\), 26 < n < 47). The fact that no distinct peak series were observed > m/z 300 in the loading plots implies that no single “pure” substance class dominates in the crystal composition. This result is consistent with TOF-SIMS images of wax structures on bitumen surfaces, and therefore, we hypothesize that the high molecular weight substances were a mixture of paraffins and branched waxes with a range of naphthenic ring systems.

In an alternative experiment, the top of the glass bell was loaded with a droplet of water in order to create an atmosphere of saturated water vapor (~27 mbar) above the oil film. The water activity of a saturated water vapor equals 1, which is similar to the water activity of pure liquid water and might mimic a first step to the formation of an oil–water interface. The result was a completely homogeneous image without any structural features. The adsorption of a (mono)layer of water apparently prevented the accumulation of very hydrophobic alkane-like molecules at the oil–water vapor interface.

Only the most polar oil showed phase segregation of paraffin/waxes at its oil–gas interface. This implies that the segregation process only sets in when the difference between solubility parameters of two classes is substantial, i.e., in this case the bulk of the polar oil versus paraffin/waxes that show hardly polar nor hydrogen-bonding interactions. In addition, the chemical potential imposed by the gas phase was also of importance. The given examples open the perspective that crude oils do not behave as dead fluids but that their constituents react in a sensitive way to their environmental conditions.

**CONCLUSIONS**

TOF-SIMS imaging was found to be a suitable technique to study the molecular composition and molecular speciation at the interface of gas and liquid crude oils. In order to conserve the natural occurring molecular interactions between oil constituents as much as possible only nondiluted oil samples were used. First, a fresh oil–gas interface was created that was exposed for various incubation times to an air, oil vapor, or water vapor atmosphere. Then, the incubation was quenched by exposure of the liquid crude oil sample to vacuum, which resulted in a rapid increase of the viscosity of the residual oil. This effectively fixed the spatial positions of the oil constituents in the nonvolatile residue. Finally, the sample was introduction into the high vacuum of the mass spectrometer. The inevitable loss of volatiles was quantified by GC×GC. The quantification aided the interpretation of the mass spectra and revealed that all TOF-SIMS mass peaks below m/z 226 had to be fragment ions.

The mass spectra of three distinct oils were evaluated. All crude oil spectra looked very similar to each other in the low-mass range (<m/z 226) and showed abundant generic fragment ions that were very similar to those observed on electron ionization mass spectrometry. Mass peaks in the higher mass range were either fragment ions or (pseudo)molecular ions that were formed by chemical ionization processes. The three investigated oils showed distinct distribution patterns of the medium and high molecular weight compounds, but the absolute TOF-SIMS signal in these regions was lean and TOF-SIMS lacked the mass resolving power to identify the elemental composition of these mass peaks.

TOF-SIMS images gave fundamental insights in the dynamics of molecular arrangements at the oil–gas interface. The images of the polar oil preparations showed that the arrangements depend on the composition of the gas phase, which indicates that the interplay of the cohesive molecular forces between oil constituents was very sensitive to external environmental conditions. Changing the gas composition from saturated water vapor to air to oil vapor resulted in the formation of none, to feeble patches, to crystalline structures, respectively. Principal component analysis of the images showed that it was hydrophobic, most likely paraffin or wax, compounds that segregated from the bulk at the oil–gas interface.

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Notes
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