

AFM Characterization of Organic Deposits on Metal Substrates from Mexican Crude Oils

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Atomic force microscopy (AFM) has been used to investigate eight different Mexican crude oils in the form of deposited films on metal substrate. Most oils had reported asphaltene deposition problems during production. Two other techniques related to hydrodynamic size determination were applied: light scattering and HPLC-SEC. According to the observed AFM surface morphology characteristics oil films were classified and grouped into distinct groups. Some had dense population of 40–200 nm particles, while others had larger discoid features and smaller particles. Light scattering analysis indicates observed particles to be organic as they disappear upon dilution with toluene. Correlation between the oil film AFM morphology and physicochemical properties of the oil did not reveal a simple relationship. Indeed, oils with similar bulk fluid properties show different morphology as films. With respect to the crude oil instability and the well-deposition problem, it was found that five of the investigated oils (unstable) with known problems of asphaltene deposition during production, contain spherical or discoid nanoparticles in the range of 35 to 500 nm. Films prepared from the stable oils possess apparent two-dimensional (2D) characteristics (spread over the substrate) without particular features. Detail of AFM analysis show that oil instability can be related to films and oils with higher density of particles, and films with larger particles. It emphasizes AFM, as a technique potentially useful for the well-deposition problem detection. HPLC-SEC data show that oils from similar geographic zones have similar fluid properties in terms of composition and hydrodynamic size distribution but on the other hand could display different AFM morphology features. The results show that AFM is a promising tool for the oil film characterization and determination of surface properties, which may lead to development of a better understanding of well-deposition and adherence.

Introduction

Crude oil is composed of hydrocarbons ranging from methane to molecules with more than 100 carbon atoms. Typically, as most natural products, large amounts of nitrogen, oxygen and sulfur as well as trace metals, are present in the oil. Hence the complexity of crude oils is almost infinite counting the numbers of possible isomers in the system. Therefore generic fractions are used to describe or simplify the understanding of the oil composition. Petroleum asphaltenes are a generic fraction of crude oil that precipitates, by definition, by addition of *n*-alkanes, such as pentane or *n*-heptane. Content of asphaltene in crude oil may range from almost zero to more than 20% of the total oil. This complex fraction consists of the highest boiling material that always remains in the distillation residue.¹ Unwanted separation of asphaltenes may take place in most processes causing large economic losses. This has been seen in

oil recovery operations where accumulation of small amounts of asphaltenes can cause well plugging and fouling of surface facilities (separators etc.); during transport and storage by formation of sludge; and during refinery operations by fouling of separators, fractionation towers, and heaters.² In general, the problem is related to the phase separation and the surface adhering processes; however, the exact mechanisms are still not revealed, in part due to complex composition and unknown properties of the asphaltene material. The molecular structure features of asphaltenes still remain speculative, although many hypothetical models have been proposed. These structures often consist of condensed aromatics regions (3–6 rings) which sometimes are linked to other aromatic “islands” by alkyl chains or heteroatom bridges.¹ There is however no exact knowledge of this. Experimental evidence shows that these molecules exist in solution and maybe also in crude oil as colloidal aggregates, which upon destabilization can associate into larger flocs that eventually can precipitate.³ Among other techniques

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Table 1. Selected Properties of Oils Investigated

oil	density at 25 °C	viscosity, cP 25°C	asphaltene <i>n</i> -heptane, IP-143	vanadium, ppm	wax, UOP, % w/w	reservoir, <i>P</i> , <i>T</i> , bar, °C	bubble point pressure, bar	stability, ^a observed
JU	0.824	NA ^b	0.2	NA	NA	685; 154	254	instable
TC	0.831	5.9	0.52	2.0	2.91	688; 150	257	instable
P	0.836	4.7	0.73	2.5	4.23	919; 147	324	instable
C1	0.852	11.2	3.08	19.7	5.60	973; 137	185	instable
SG	0.858	1.3 ^c	NA	NA	NA	380; 127	297	stable
Y3	0.863	8.7	2.71	20.6	5.49	979; 137	203	instable
B1	0.919	NA	NA	NA	NA	312; 117	88	stable
KU	0.980	14317	10.94	NA (high)	NA	171; 115	NA	stable

^a Reservoir experience. ^b NA: not available. ^c At 125°C.

molecular weight measurements indicate a tendency of asphaltenes to associate into colloidal like structures, even in dilute solution. Colloidal size, determined using light scattering techniques^{4–6} and dielectric spectroscopy,⁷ is in the range from a few to 250 nm, depending on the state of stability of the system.

In terms of oil production well deposition, some reservoirs may only have problems showing up as solid precipitation in surface separators, whereas others may have severe problems giving rise to plugging of well bores.^{1,8} The latter is assumed related to deposition of the asphaltene particles onto well bore tubing metal surface. In the present paper, the surface morphology characterization of the deposit of crude oils on gold metal surface was performed by atomic force microscopy (AFM) as an initial step toward understanding the deposition. The oil samples were collected from eight different locations in Mexico. Most of these reservoirs suffer from well-deposition problems in different extent. The aim of the work is to see whether a specific pattern in the surface morphology of the oil deposit was formed on our model metallic substrate and if this could be associated with problematic oils. The results were compared with known physical and chemical properties of the investigated oils and reservoirs.

Atomic force Microscopy⁹ is a highly sophisticated and powerful technique for surface morphology characterization. It is based on imaging (visualization) of the sample surface with high resolution. From work in other fields than petroleum science it is well-known that AFM offers very useful data on a surface roughness, surface profiles, distributions and determination of particle size on the surface on microscopic and atomic level, etc.^{10,11} Since asphaltene particles (micelles, aggregates, floccs, and superfloccs) have been reported in the previous literature to have size in the range from a few to 250 nm,¹² the AFM seems to be an obvious choice for such type of studies.

The technique has a growing interest in the petroleum related science, and have been used in a number of studies where asphaltenes adsorbed from solution.^{13–15} Most efforts have been related to wettability of surfaces and alteration of this by adsorption of petroleum heavy ends. However, to our knowledge this is the first study of this kind where oil films containing instable asphaltenes are directly deposited on the metal surface and visualized by AFM. Comparison with published petroleum related AFM images will be made below.

Experimental Section

The stabilized dead oils were analyzed as received, possibly with water dispersed as well as presence of mineral matter. However, only SG-oil had shown a visible sign of the water separation (approximately 5% vol) over a 6 month period after the experiment were performed and therefore water must have been present as an emulsified phase (water-in-oil). The Oliensis spot test on filter paper indicated the presence of solidified material in all samples except the SG oil. Oils marked as KU and B1 are heavy viscous oils. The samples came from similar geographic zones, in the south and the Gulf of Mexico. In the following discussion, it is important to note that oils: P, C1, and Y3, come from the same geographic area and that oils C1 and Y3 may have the same source rock. Oils JU and TC, are from very close reservoirs, as are KU and B1. All PVT properties used in our study were taken from standard PVT internal IMP reports (Table 1).

Apart from standard analysis of oil properties (density, viscosity, asphaltene, wax, and vanadium content), based on ASTM and IP methods, the oils were analyzed using HPLC size exclusion chromatography (SEC) in order to show hydrodynamic size and association affinity of the samples in dilute solutions. The equipment consists of a Waters 600 Controller, a 717 Plus auto-sampler, 996 Photodiode array detector, and a 410 refractive index detector. The column was a mixed gel column with THF eluent. This allows short retention time and separation of large ranges of molecular weights. The column was calibrated regularly with polystyrene standards to check retention time repeatability.

The presence of larger particular matters of the nanometer size, was examined using a Brookhaven zeta plus analyzer and a toluene dilution (1:60 vol) procedure to obtain a reliable result for these opaque samples at a scattering angle of 90°. The viscous oils K and B1 were diluted more than 200 times to reduce opacity hampering the measurements. Fluorescence effects were not taken into account in the interpretation and the technique was only assumed to give a semiquantitative picture of the particles in the solution. This analysis was especially important as the AFM method does not reveal the

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nature of the particles which in crude oil could be organic, salt, clay, or other fines from the reservoir.

To prepare a solidlike sample for AFM analysis, a drop of oil was placed on the perfectly flat metallic substrate (see below) and heated to 80 °C during 24 h. From experience, during this time, almost all material up to *n*-heptane and parts of the sample up to *n*-decane will evaporate, allowing the formation of a more stable surface film and hence enhancing the imaging of the particles. Hence, the heavy ends were left on the surface in the form of a solid like residue. No steps were taken to avoid oxidation of the oil sample during the evaporation, and therefore, the sample may be slightly oxidized. It is believed that this will not alter significantly the morphology that is present initially in the spread liquid film as solids are already present in most of the oils. Also the heat treatment is mild considering the chemical alteration of asphaltenes and resins. The solid like films had thicknesses of a few micrometers.

AFM (Nanoscope III, Digital Instruments, USA) was used for visualization of the oil films deposited on the gold surface. Imaging was performed ex-situ under laboratory atmosphere conditions, with operating the AFM in the so-called "tapping" mode.¹⁰ In short, the "tapping" mode provides less contact between the AFM tip and the sample, which leaves sensitive samples in an intact form. Imaging was performed using standard silicon probes (TESP-tips) provided by Digital Instruments. Tips were 125 μm long and had typical resonance frequencies between 294 and 375 kHz. Typically, scanning started at 20 μm × 20 μm area, and gradually the image size was reduced to 1 μm × 1 μm. All AFM images were recorded during slow scan rate (1 Hz), to avoid sample damaging. Hence impact neither on tips nor samples was noticed. Images have been recorded in the height and the phase mode, simultaneously. The height mode is related to the sample surface topography. The phase sensitive imaging maps the phase of the cantilever oscillation during the tapping mode scan, and this detects variations in adhesion, friction, stiffness, viscoelasticity and similar mechanical properties^{16–20} of the imaged area. In this study, we noticed that images with phase contrast provide better resolution, which helps to determine the final shape and dimensions of nanoparticles in the oil film. However, as reported before, monitoring changes in the phase frequency or amplitude of the AFM response, often leads to data that are complementary to topographic information.²¹ To satisfy the representative nature of our analysis, five different places were checked on each sample. Images presented in the paper are shown in the top-view mode. Quantitative evaluation of particle dimensions, and average film surface roughness were performed using the Nanoscope software.

As a substrate for the oil film gold coated glass samples were used. Gold is a noble metal, sufficiently inert to not chemically interact with oil components. The gold sample consists of a 200 nm thick film of very pure gold evaporated onto a special heat resistant glass (BerlinerGlas KG), with a 2 nm thick Cr adhesive undercoating layer. It is perfectly flat, with large terraces of the (111) orientation, created during annealing in a hydrogen air flame at orange/yellow heat for a few seconds. This annealing treatment was previously demonstrated to

produce a high quality and perfectly flat surface with micron size (111) terraces.^{22–24}

All chemicals used in our study were HPLC grade (Merck).

Results

To present our results in more systematic and comparable way, AFM images of the same size (ca. 4.6 μm × 4.6 μm) were presented. Also to point out difference in morphology between oil films and the gold substrate, AFM images of the clean substrate are presented in Figure 1. The gold substrate consists of large, micron size, grains with characteristic sharp edges. The image in Figure 1a, is recorded in a height mode and shows typical morphological properties of such surface. The phase image, presented in Figure 1b, shows the same surface but with higher resolution. Both type of images show that the gold substrate consists of large grains with top flat terraces and clear grain edges.

In comparison, the oil covered substrate morphology is very different, heterogeneous and with many different features. In general, the oil films possess a non specific morphology with simple geometrical features (spherical, etc.) (see Figures 2–9), and with no evidence of sharp grains and clear grain edges characteristic of the gold substrate. This has much sense since oil films prepared on the gold substrate were eye-visible and at least a few microns thick. Besides the clear difference between surface morphology of clean and oil coated substrates, it is also easy to see that oil films from different locations differ in morphological characteristics. Although, shape and size of the surface features in the AFM images for each of the investigated oil seem to be different, a detailed analysis of all images indicates that samples can be divided in characteristics groups: (1) oil films which contain well defined spherical particles (Figures 2, 3, 5, and 8 corresponding to samples: C1, JU, TC and SG, respectively) and (2) oil films consisting of large discoid particles (Figures 6 and 7, corresponding to P and Y3 samples, respectively). Oils B1 and KU may as discussed below be part of the same group or differently grouped: KU in group 1 and B1 in a third group of very dispersed matter according to both types of images recorded. One should be careful with SG which as mentioned did contain fairly large amounts of dispersed water.

The image in Figure 2 (C1 sample) reveals a surface containing numerous spherical particles, with rather uniform size variation between 40 and 200 nm with an average diameter around 80 nm. The surface density of the observed particles appears to be different for each sample; i.e., sample C1 (Figure 2) is about three times more populated with spherical features than JU, in which one may also see the features of the substrate (Figure 3). For JU this could be expected as recent investigations of in-situ depressurization of the oil indicated a natural asphaltene deposition less than a

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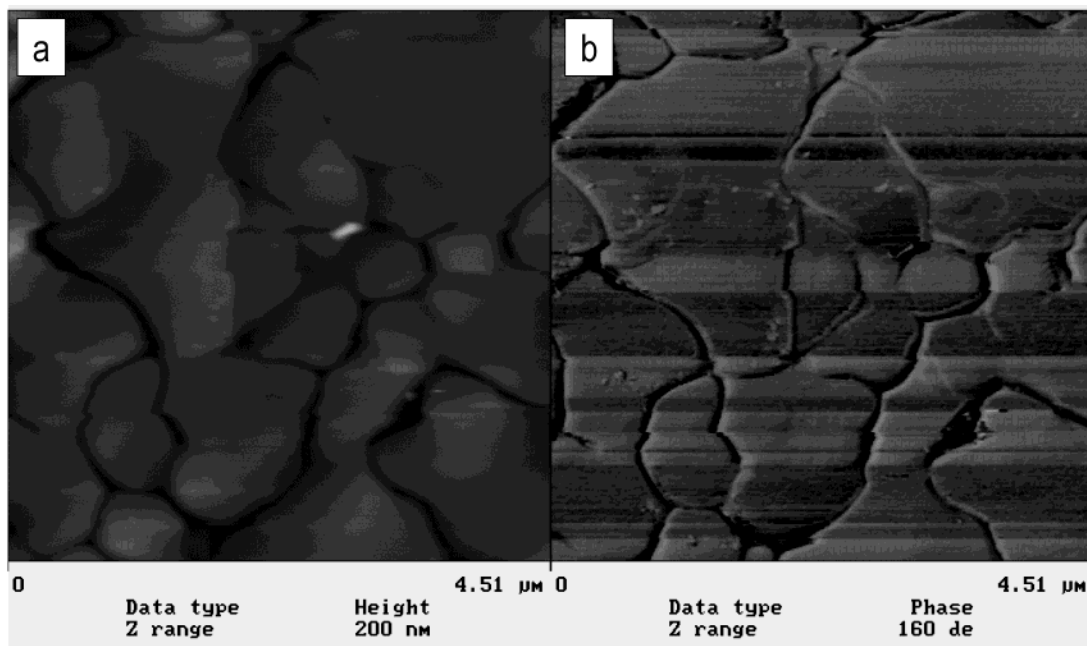


Figure 1. AFM image ($4.51 \mu\text{m} \times 4.51 \mu\text{m}$) of the gold substrate: topographic height mode (a) and phase mode (b).

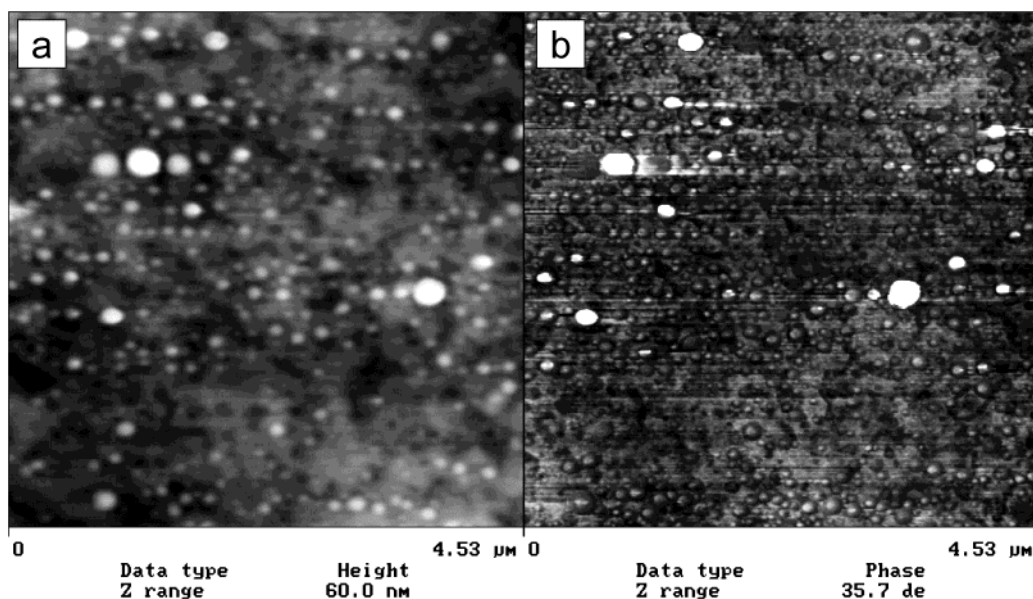


Figure 2. AFM image ($4.53 \mu\text{m} \times 4.53 \mu\text{m}$) of the oil film C1 spread on the gold substrate: topographic height mode (a) and phase mode (b).

100 ppm.²⁵ In all samples in group 1 it seems that the observed particles do not show tendency toward interparticular association like cluster formation, as recently reported for asphaltenes from solution on mica.³³ In-

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terparticle interactions are apparently rather weak and therefore in all images mainly isolated spherical features were observed.

The surface of the KU film (Figure 4) is of similar characteristics. It consists of spherical particles whose size varies from 60 to 100 nm (small) and 300 nm to 500 nm (large). The phase image resembles that of B1 (Figure 9) that also as KU belongs to the Maya crude oil family. Especially KU looks as blisters on a soft surface. Comparing the height mode of the two oils some differences that indicate that KU is more particle-like are observed. Hence the grouping is not straightforward.

The oil films of P and Y3 samples mainly consist of discoid (disklike) shaped features. As can be seen particularly in Figure 6b (phase image), the surface film seems to be more compact, and covered with numerous discoid terraces, with sizes varying from 35 to 250 nm

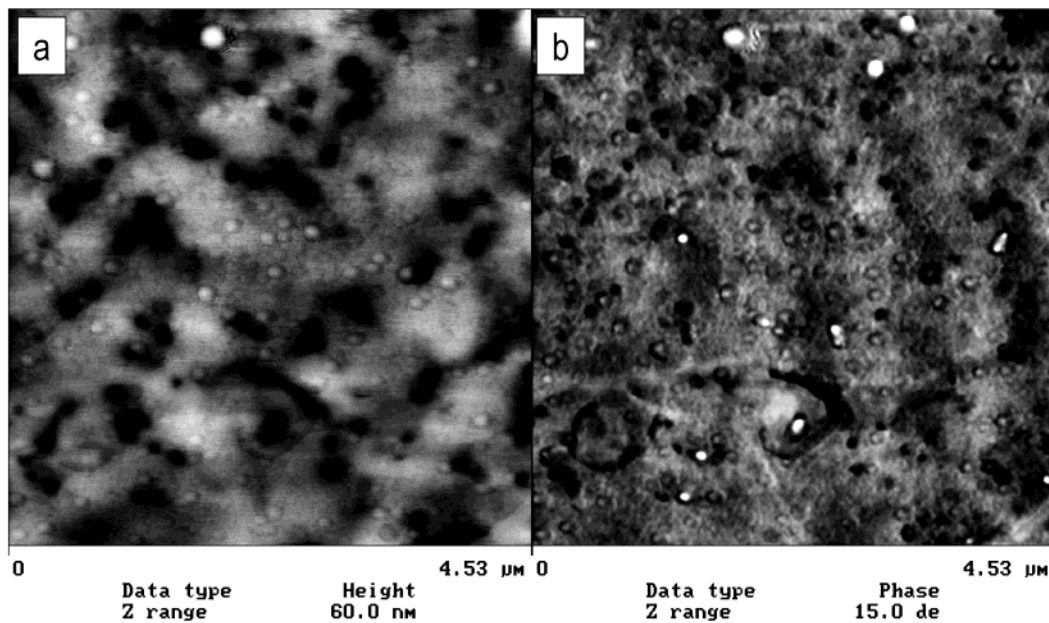


Figure 3. AFM image ($4.53 \mu\text{m} \times 4.53 \mu\text{m}$) of the oil film JU spread on the gold substrate: topographic height mode (a) and phase mode (b).

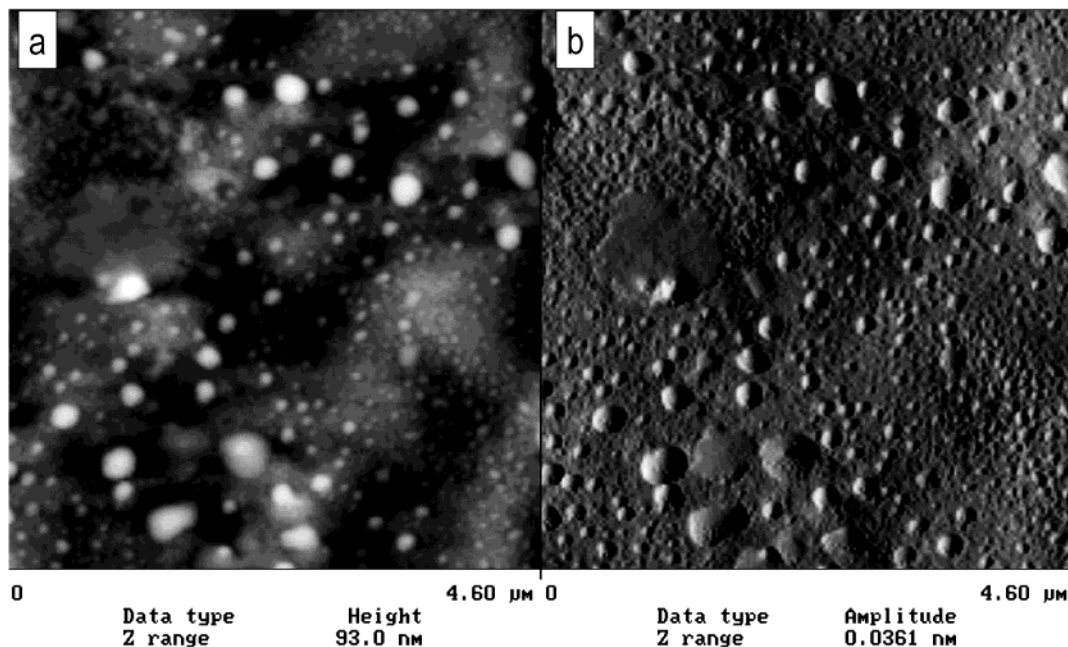


Figure 4. AFM image ($4.60 \mu\text{m} \times 4.60 \mu\text{m}$) of the oil film KU spread on the gold substrate: topographic height mode (a) and amplitude mode (b).

(diameter). Indeed, some of them are much larger, which may be interpreted as a result of the interparticle aggregation at the film surface. The thickness of the discoids is only about 0.4 to 1.5 nm, which is the range of a few asphaltene monolayers (regarding to models presented in ref 25). Image of the Y3 sample (Figure 7) reveals the presence of spherical features too, but in a much smaller extent than compared to oil P.

The third group which could be formed is represented by SG and B1 samples (Figures 8 and 9, respectively). The AFM tip-sample interaction (observed during measurements) indicates that the surface of these samples is somehow softer than that of group 1 and 2. During imaging of these samples, attraction between the surface and the AFM tip was noticed. In images in

Figures 8 and 9, the samples appear to be covered by numerous relative small particles with no defined shape. The particle density is large, but the images still reveal that individual particles could be recognized. Regarding the uniformity of the observed film, it seems that this corresponds to a flat uniform film. It should be remembered that oil SG contained a high level of emulsified water that may still be present in the film after the heat treatment.

Table 2 shows major findings based on AFM observations and result of quantitative analysis using the obtained images and the appropriate software. During a quantitative analysis the size of all observed features were evaluated regardless of their shape. The biggest features (particles over 300 nm in diameter) were found

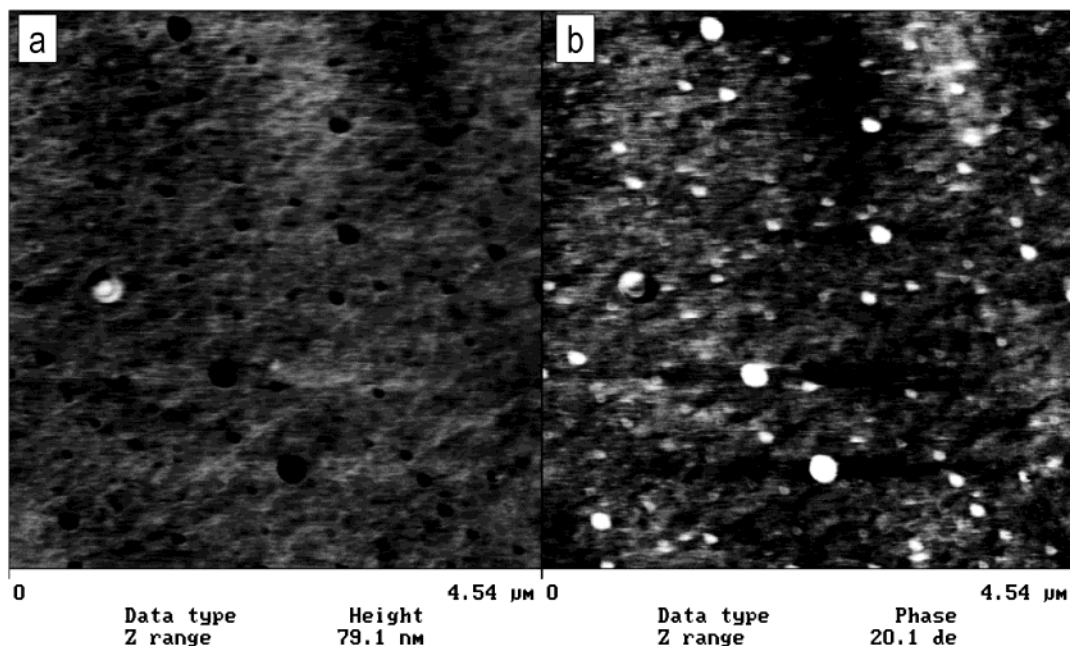


Figure 5. AFM image ($4.54 \mu\text{m} \times 4.54 \mu\text{m}$) of the oil film TC spread on the gold substrate: topographic height mode (a) and phase mode (b).

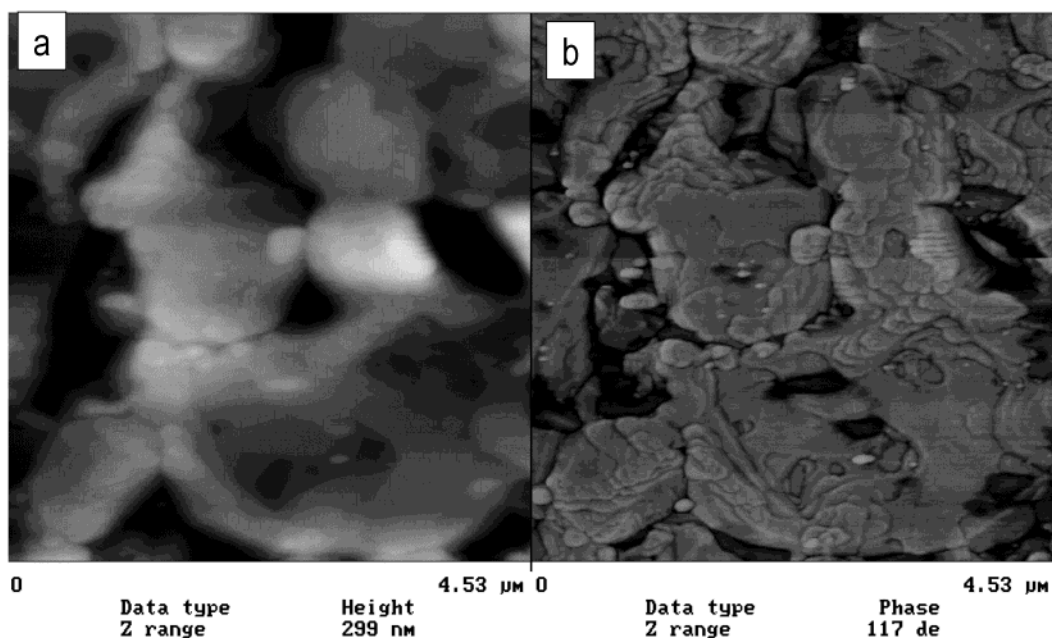


Figure 6. AFM image ($4.53 \mu\text{m} \times 4.53 \mu\text{m}$) of the oil film P spread on the gold substrate: topographic height mode (a) and phase mode (b).

at surface of KU, Y3, and C1 films. However, particles in C1 and KU samples were spherical, and in the case of Y3 film, it was a mixture of spherical and discoid features. Since we believe that different morphology of the oil films indicates different mechanisms during film formation, which is controlled by intermolecular and interparticle type of interactions, we like to propose that the presence of larger spherical particles is a sign of the easy aggregation among molecular material. In particular, it can be aggregation of the asphaltene material. Note, according to the literature,²⁷ asphaltenes can aggregate into super micelles (10–20 nm) or even giant super micelles (200–2000 nm). The values found here are in the same order of magnitude reported in various

studies using scattering techniques such as SANS and SAXS as reviewed and discussed by Espinat and co-workers.²⁸

To evaluate oil film morphology even more quantitatively, the surface roughness analysis on all oil samples was applied. In the ideal case, one supposes that surface roughness is a function of the film particle size. However, association between different components could significantly alter roughness and other morphological properties of the film surface.²⁹ Therefore we performed the roughness analysis, to explore a possibility of detecting changes in films due to association between particles in the oil. The analysis was based on a calculation of a standard deviation of all height values

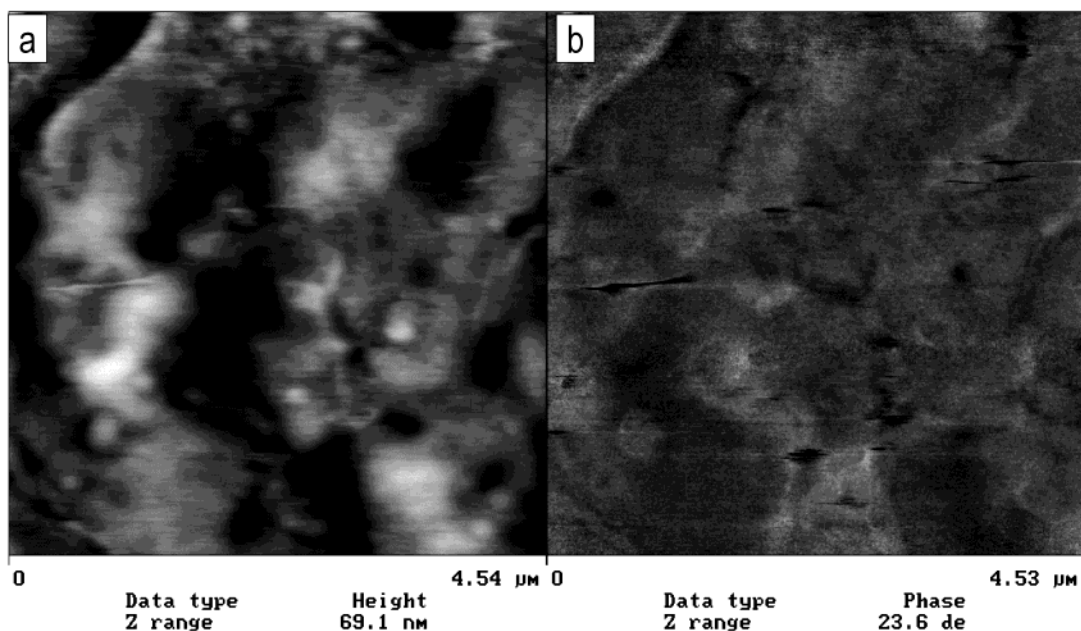


Figure 7. AFM image ($4.54 \mu\text{m} \times 4.54 \mu\text{m}$) of the oil film Y3 spread on the gold substrate: topographic height mode (a) and phase mode (b).

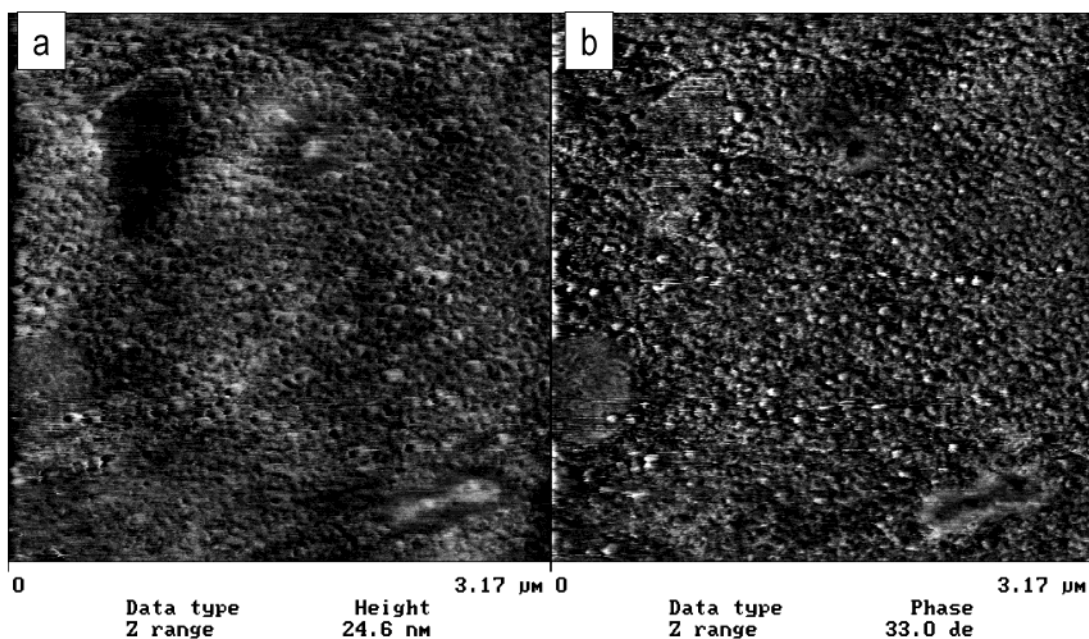


Figure 8. AFM image ($3.17 \mu\text{m} \times 3.17 \mu\text{m}$) of the oil film SG spread on the gold substrate: topographic height mode (a) and phase mode (b).

within the given (imaged) area, and expressed as the root-mean-square RMS[Rq] average of the surface roughness factor. For more details, see previous literature on roughness measurement by AFM.^{30–35} Results show that for the majority of films (C1, JU, TC, and Y3) RMS[Rq] is in the narrow range from 3.40 to 4.67 nm. In comparison with recent data by Lord and Buckley²⁶ the films are less rough as the asphaltene patches on mica reported to be about 8 nm. Indeed, AFM images in this work reveal that films are spread over the surface in a rather homogeneous manner. Out of this range is SG

with a very low value (the uniform film), and three other samples (KU, P, and B1) with rather high values. Again KU and B1 are very similar which could group them together as heavy oil films. But, surprisingly, particles in the KU film are much bigger than particles in the B1 film. The SG film is very flat and consists of particles of narrow size distribution, which gives very low surface roughness. The reason for the very high surface roughness of the P film is a tendency to form multilayers, which clearly have been resolved in AFM images (Figure 6). They were built one over another in this way that increase in the surface roughness is inevitable. So far, it is not clear to us, how to relate the film surface roughness to the other oil film properties. More research in this direction is in progress.

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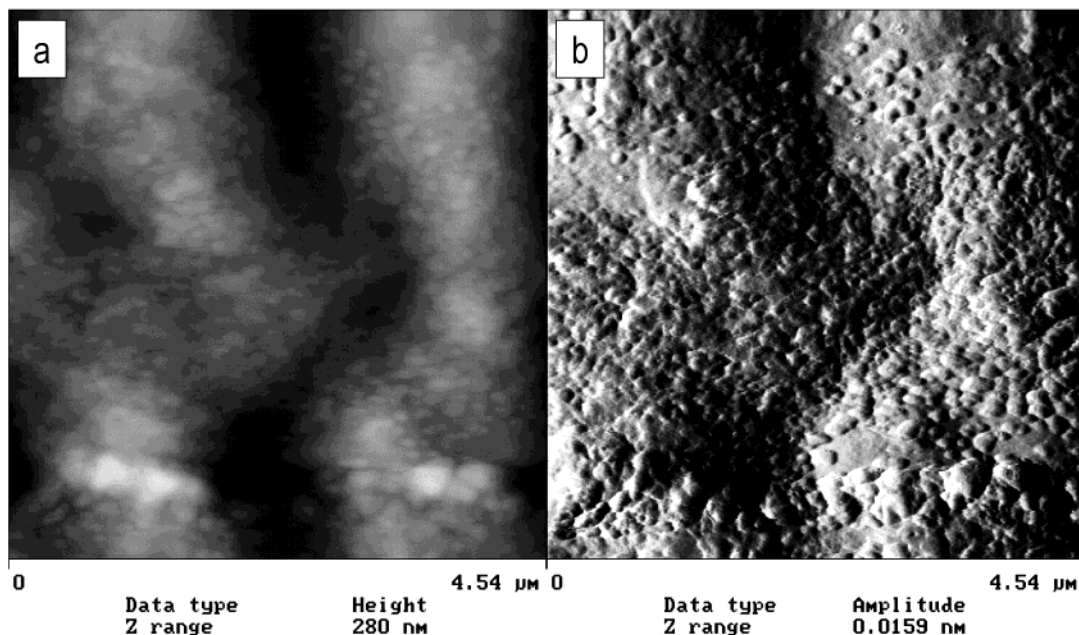


Figure 9. AFM image ($4.54 \mu\text{m} \times 4.54 \mu\text{m}$) of the oil film B1 spread on the gold substrate: topographic height mode (a) and amplitude mode (b).

Table 2. Results of the AFM Analysis

oil film	particle observed shape and size/nm	RMS[Rq]/nm
C1	spherical, 80–300	4.01
JU	spherical, 140–145	4.18
KU	spherical, small 60–100 large 300–500	12.30
TC	spherical, majority around 100 and few around 250	4.67
P	discoïd, multilayers diameter: 35–250 thickness: 0.4–1.5	21.27
Y3	discoïd and spheres: 140–300	3.40
SG	half-spherical, 75–80 (uniform distribution, densely populated)	1.04
B1	half-spherical, 100–200 (like SG)	13.12

To place the oils in the industrial perspective the oil instability in terms of asphaltene phase separation and relation to the well-deposition problem should be clarified. For all samples we had access to field case experience such that all oils marked as instable indeed were instable. Thermodynamically one of the reasons for the instability of the oils examined are the large difference between original reservoir pressure and the bubble point pressure where the dissolved gas is initially liberated combined with the low in-situ density of the oil, as this is related to the changes in thermodynamic equilibrium conditions of the reservoir fluid during production. To illustrate this, our data has been plotted in Figure 10 as ΔP versus in-situ density (measured on preserved bottom hole samples) as proposed by De Boer et al.³⁶ The supersaturation lines, which were calculated originally from the Hirschberg approach,^{37,38} have been redrawn for an average asphaltene composition without

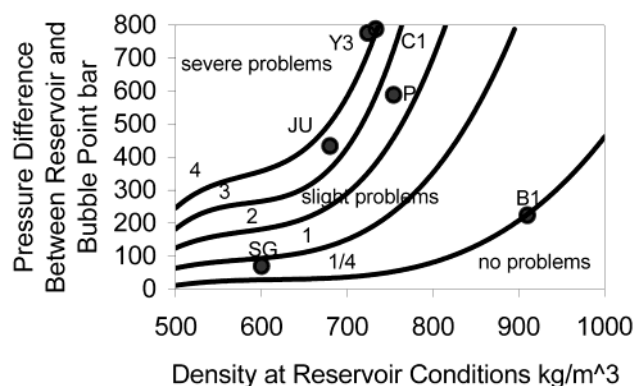


Figure 10. de Boer plot with generalized saturation lines (large numbers high supersaturation). See ref 36 (de Boer 1995) for details.

taking any temperature effects into account. For details see the original work of De Boer et al.³⁶ Five out of the eight examined oils in this work are instable in terms of the asphaltene phase separation during production depressurization, although they at the actual reservoir conditions exist as stable solutions or dispersion. They fall into the range of high supersaturation at the bubble point and severe precipitation problems should be expected. In this context we should strictly distinguish between precipitation and deposition, and the de Boer plot only is related to the thermodynamic phase separation. Asphaltic matter may precipitate but not adhere to surfaces. Adherence must therefore be related to the surface properties of the formed particles. Oils SG and B1 fall outside the problematic region and no data were available for KU and for TC regarding the in-situ density at reservoir conditions. However, TC experience a large pressure difference as seen in Table 1 and have reported problems, while KU has no problems as a typical Maya crude. Note that SG has a very low in-situ density.

Before trying to understand the observed surface morphology in terms of correlations with bulk properties

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Table 3. Results of Light Scattering Particle Sizing, and HPLC-SEC Results

	particle size, ^a nm	SEC front min, 500 nm	SEC peak min, 500 nm	area ratio ^b A350/A500
JU	0* ^c	7.77	9.55	18.4
TC	0* ^c	7.77	9.54	19.4
P	0 ^d	7.77	9.39	14.3
C1	0 ^d	7.71	9.20	12.1
SG	NA ^e due to water	7.77	9.35	22.4
Y3	0* ^c	7.71	8.98	11.3
B1	230 ^f	7.26	8.50	8.0
KU	0 ^{c,f}	7.26	8.63	8.8

^a The particle size lower limit is 2 nm. ^b Absorbance ratio below SEC trace nm indicated. ^c Strong but instable correlation observed 10 min after sample preparation, none after 40–60 min. ^d Constant correlation function immediately after dilution. ^e NA: not available. ^f Diluted ca. 200 times.

of the oils, which could be assumed to play a role, an indirect attempt to characterize the nature of the particles was made. By using light scattering directly on the oils and diluting the samples with a solvent it can be observed whether the solvent affects the state of the particles. Toluene should dissolve all normal organic deposits such as asphaltenes. At the same time the additional particle characterization may help in understanding the semiquantitative AFM images. The classical “spot test” revealed that solid particles, seen as dark rings inside the oil spot, were present in the instable oils. The light scattering showed that on dilutions of the oils in toluene (1:60) only the stable oil B1 had consistent apparent particulate matter with sizes in the range of 200 nm. Note that AFM also recognized particles in the range of 100 to 200 nm in the B1 film. The other oils showed a large spread in data. Particles were present just after dilution and disappeared within a series of measurements about 1 h after sample dilution. These also showed auto correlation functions deviating from a constant value indicating that there exist indeed particles in some of the oils: i.e., oil C1 with high density of spheres (see Figure 2) immediately dissolved into the toluene and zero count of particles were given with a constant value for the autocorrelation. Oils showing deviations from constant autocorrelation function are marked with an asterisk in Table 3. The results confirm indirectly that spheres and other features observed in the oil films by AFM are mainly due to organic matter which can be dissolved in toluene to sizes smaller than the 2 nm lower limit of the light scattering equipment. Wax crystallisation is another type of solid formation that is possible to observe in AFM at room temperature conditions. Can one mistake asphaltenes for wax? Since wax consists mainly of linear long chain *n*-alkanes that crystallize upon dilution, this is not material which is likely to form spheres upon cooling and crystallization, but rather needlelike crystals.³⁹ Therefore, taking into account our experimental conditions, especially room temperature, we can almost for sure out rule that particles observed by AFM are related to wax deposition and hence it must be asphaltenic. This is also confirmed in other works.²⁵

The next step was to correlate the AFM observations with other physicochemical properties of the investi-

gated samples. This is not trivial due to the large difference in both chemistry and structure of oils, and the fact that bulk and surface properties are compared, as AFM reveals properties of the top layer of the solid or quasi-solid oil film surface only. It should be remembered that this is the first attempt to compare such a large number of different oils by AFM. However, lack of data related to the surface properties of the oil films as well of surface interactions between oil and metal substrate, is obvious, and therefore an attempt is made here. The data used herein has been obtained from other research projects at the Mexican Petroleum Institute. Hence the data set is unfortunately not complete, and only qualitative discussions will be made on the bases of the available data. Data are given in Table 2.

For the instable samples showing spherical particles C1, JU, TC there seem to be a relationship between asphaltene content and the density of particles: In the images for C1 and JU, it can be seen that concentration of spherical particles is at least 2 times higher in the C1 film. Technically the C1 oil containing larger number of spherical particles presents a major problem during production, while the problems are smaller for JU and TC oils, with less particles. If we include KU and B1 in this group both being Maya crudes of very high asphaltene content we can extend this correlation. These two oils are quite similar in composition and the HPLC-SEC analysis indicates that they display the same hydrodynamic aggregate size when dissolved in THF. However, the two oils are not instable and therefore must fall in another type of thick film textures.

A closer examination of these two oils also shows some differences in the shape of the features observed. For KU this is spherical while for B1 it looks more like irregular shapes of smaller average size. Y3 also has high viscosity and content of asphaltene of the same level as C1, but AFM imaging reveals the surface morphology to be dominated by discoid features with some particles observed in the height mode. This could indeed be related to the very low content of matter precipitating in-situ from this oil, showing that a correlation between total asphaltene and in-situ precipitated mass is not possible.²⁵ Regarding these examples, it is obvious that straight correlation between the AFM results and normally available oil physical and chemical properties is difficult to establish if possible at all. However, as discussed below the AFM images reveal some crucial differences among oils that all show deposition problems. These features cannot be explained by thermodynamics (such as the de Boer plot) and therefore should be sought in the colloidal stability. More detailed studies are in progress to resolve this issue. The SG oil, as a special case, which is showing very small half spheres with sizes in the range of 75–80 nm in AFM images, has been known to exhibit problems with *inorganic deposition* and as well did show large amounts of emulsified water at the point of measurement. From the SEM measurements it has been shown that at least emulsified water droplets in crude oils have diameters from about 0.1 μm and up.⁴⁰ This is not in agreement with the observed pattern but

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as no technical problems with organic deposits are reported for this field, it is assumed that the particles seen must be inorganic or water.

In conclusion, presence of spherical or discoid features (aggregates) in the oil deposit indicates well-deposition (production) problem. However, this relation is not simple, and it seems depend on many parameters such as: particle size, shape and particle density. Therefore, the AFM analysis of the oil samples may provide a simple way of evaluating well-production problem by imaging the presence and extent of particles without the generally employed separation for these from the oil.

Another issue is the possible impact of the sample preparation for the AFM analysis on the quality of the oil film. The technique of evaporation of the light-ends of the oils at 80 °C to obtain a stable film, certainly affects the composition as well as the concentration of the particles on the surface. At 80 °C most of the components boiling below *n*-heptane will be removed. This will leave, especially for the light oils, more concentrated film. As the light components are assumed to cause the precipitation one may expect that the evaporation will have the reverse effect. Under the given experimental conditions the chance of having oxidation of the oil is rather large. This is known to cause formation of *n*-heptane insolubles⁴¹. Evaporation of droplets from surfaces may take place either through constant contact angle θ or constant contact radius R ⁴² depending on the substrate-liquid interaction. If a nonwetting interaction is in play and $\theta > 90^\circ$ the radius will change and θ will remain constant and the reverse is seen for wetting interactions.⁴³ For the very viscous oil KU, where surface is dotted with droplets (size: 2–3 μm) in a regular manner, it could indicate that a certain point a constant contact angle evaporation took place leading to rupturing of a thick film, or the presence of water in a thick viscous film. Understanding this mechanism will be very important in the assurance of a uniform film preparation technique giving comparable results among different oils.

To get more information on the sample hydrodynamic size distribution, and to get insights into the distribution of molecular types, the oils were subject to size exclusion chromatography (HPLC-SEC). This method has been shown at least for asphaltene samples to reveal the tendency to association and distribution of species⁴⁴ and references herein. Chromatograms are given in Figure 11a,b for a detector wavelength of 500 nm. The results match very well with the geographic position in the sense that oils B1 and KU are from the same area and show similar chromatographic profiles, JU and TC are neighboring field, as well as Y3 and C1. Therefore, one may expect similar behavior partially due to similar source rock composition. In Table 3, the main features are given: the peak and front retention times, as well as the ratio between areas below the distributions obtained with two wavelengths. The obtained magnitudes indicate that KU and B1 have the highest molecular weights, which leads to the assumption that the

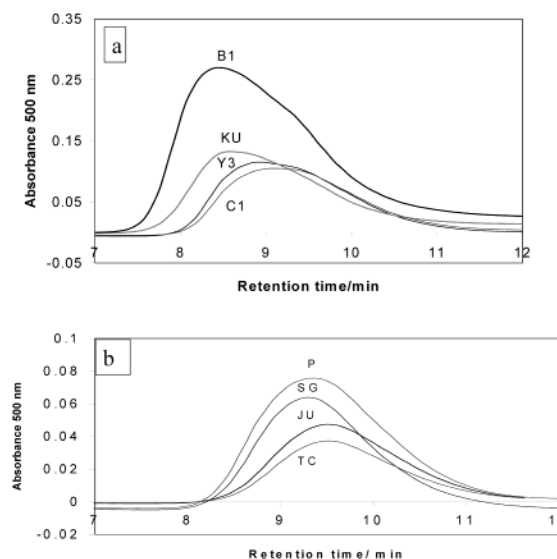


Figure 11. HPLC-SEC traces at 500 nm absorbance for oils: SG, P, JU, TC (a) and for oils: B1, KU, Y3, C1 (b), respectively.

bimodal nature comes from the high asphaltene content of these two oils. The A350/A500 absorbance ratio besides supporting the qualitative evaluation from the chromatographic profiles, also clearly indicates on differences between SG (as a very light oil) and the other investigated oils. The absorbance ratio gives a relative indication of the difference in population of species with few conjugated bonds (350 nm) to those with many conjugated bonds (500 nm), independent of the molecular size. Again, oils KU and B1 show the highest content of complex chromophores, as seen from the low values of A350/A500 and the low front retention time for these oils. On this basis, one would expect fairly large but stable particles to be revealed by AFM. For oils Y3 and C1 with almost similar properties (Table 2), with a high probability for the well deposition problem (Figure 10), as well similarity in the HPLC-SEC analysis, the AFM shows two different types of film properties. Therefore it must be assumed they are formed by different mechanisms or from different macromolecules.

Much speculation exists on the formation of particles in petroleum fluids. We believe that the process of the sphere formation is similar to the mesophase formation during heat treatment at temperatures above 350 °C,⁴⁵ which takes place in a local region in the liquid phase, due to the free energy optimization during the phase transition process. Although the phase separates, the spherical particles do not coalesce, indicating on a certain interparticle repulsion. However, systems such as P and Y3, which show deposition of organic solids (discoid features), may have little interparticle repulsion and coalesce readily forming larger deposits. Therefore, it could be two different mechanisms in the formation of asphaltene deposit phases: (a) one where particles pack together and (b) one in which the particles are formed but because of little repulsion between these, coalescence will take place and a continuous dense deposit will be form. Understanding this will be very important in selection of inhibitor treatment procedures. In further speculations on this one may use analogies

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to colloidal stability theory. The observations made herein imply that for some systems the effective Hamaker constant in the particle interaction is small, leading to no coalescence of the dispersed particles. This takes place when particle surfaces and liquid medium (oil) are almost similar chemically. Another mechanism could be steric stabilization by adsorbed material. Obviously, according to this view, systems such as Y3 and P could have low energy barriers to particle coalescence and collision will lead to aggregation. For systems such as JU, TC, and especially C1, the energy barrier must be large, hence stabilizing the spherical particles. This however remains speculations but guides the path for our future research. Density differences between oil and asphaltene particles may be as high as 0.4 g/cm^3 and thus sedimentation will take place and particles may still adhere to metal surfaces forming surface aggregates. In respect to the well deposition problem and our observations, it should not be excluded that formation of the troublesome organic deposit on the metal substrate, is actually guided by several different and rather independent mechanisms, which can proceed with equal efficiency. The choice of mechanism certainly depends on the oil composition and oil properties. In future research visualization of the oil film formation, directly in the real time, by AFM or other SPM techniques, will help to identify and characterize such different mechanistic pathways.

Conclusions

AFM has been used to study eight different oils in the form of the deposited films on the metal substrate. According to the observed surface morphology characteristics, the oil films were divided in groups which had oil films containing: spherical particles; discoid particles and amorphous oil films, with no defined particles. Semiquantitative correlations between AFM observations, bulk properties and instability history was attempted but without conclusive results, and it was observed that oil of apparent similar chemistry (both bulk properties and HPLC-SEC derived) could give rise to different morphology in the sample films. Applying another particle size technique, light scattering, indicated that in 7 of the 8 oils particles would disappear upon dilution with toluene. However, increase in the oil

asphaltene content, does not lead to formation of particles with a preferential shape. Further detailed studies are necessary to resolve the role of asphaltenes in the formation of the observed particulate matter. A general conclusion can be drawn, that although oils may have similar physic-chemical properties, they could form deposits with different morphology (different particular matter, size and shape) indicating different mechanism of formation.

The AFM method offers a unique possibility in visualization of the particles leading to the technical problems in the oil industry without removing these from the oil. This has shown that at least two types of features can be seen which indicates that the well-deposits are formed by different mechanisms. Further understanding of this is required and may lead to an AFM technique which can be used in advising on inhibitor and remediation procedures. Also the technique has indicated that for oils showing spherical particles there was a qualitative correlation between well-deposition experience (severity and magnitude) and the density of particles observed in the AFM image. Hence potentially AFM could be developed to form a solid base for a simple technique in testing the magnitude of well deposition. As more knowledge emerge it may be possible to link knowledge of colloidal stability theory with the observations of the two types of films of instable oils.

To identify all the mechanisms and determinate conditions at which well-deposition occurs, it seems that direct visualization of the film formation by AFM, will be required. So far, our study demonstrates that AFM is a very useful tool in characterization of oil deposits at the nanosize level.

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