Asphaltene Aggregation from Crude Oils and Model Systems Studied by High-Pressure NIR Spectroscopy

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The aggregation of asphaltenes by pressure depletion both in a live crude oil and model systems of asphaltenes in toluene/pentane solvents is studied. Near-infrared spectroscopy utilizing a high-pressure NIR cell with a maximum operating pressure of 325 bar is used to study the onset of asphaltene aggregation. The NIR spectra are subject to a principal component analysis (PCA) in order to detect the asphaltene aggregation onset pressure. The effect of fluid compressibility on the NIR spectra is also demonstrated. The aggregation behavior of asphaltenes in model systems is shown to resemble the aggregation behavior for the crude oil. However, while the asphaltene aggregation in the crude oil is more or less completely reversible with repressurization, indications of only a partial redissolution are seen in the model systems. The kinetics of the redissolution is quite slow. A time of 72 h to equilibrate at the original pressure of 300 bar was required to redissolve the asphaltene aggregates formed within the crude oil by depressurization of the sample. Near-infrared spectroscopy in combination with principal component analysis is shown to be an efficient tool in detecting both bubble points and asphaltene aggregation onset pressures in high-pressure systems.

Introduction

Asphaltene aggregation problems are encountered both in the reservoir and during transport and processing of petroleum fluids. It is difficult to predict where and when in the production such problems might arise, but the consequences of unexpected asphaltene deposition can be severe, both technically and environmentally.

Due to the complex and highly polydisperse composition of the asphaltene fraction it is defined operationally as the fraction of the crude oil precipitating in light alkanes such as *n*-pentane, hexane, or heptane. The precipitate is soluble in aromatic solvents such as toluene and benzene. Asphaltenes are the heaviest and most polar molecules in the crude oil, containing larger amounts of heteroatoms (N, S, O, metals) than the rest of the components in the crude oil. The molecular weight of asphaltenes is difficult to determine due to their strong tendency to self-aggregate, but a molecular weight of approximately 1000 g/mol is commonly mentioned.[1,2]

It is generally accepted that the asphaltene molecules are dispersed in the oil by the polar molecules, aromatics, and resins, thus stating that the asphaltenes are colloidally dispersed in the crude oil.[3,4] Resins adsorb on to the asphaltene aggregates and keep them dispersed in the crude oil medium. The molecules of the resin fraction are generally considered to be smaller than the asphaltene molecules. One common definition of resins is as the fraction soluble in light alkanes such as pentane and heptane, but insoluble in liquid propane.[2,5] The stability of this colloidal solution of asphaltenes dispersed by resin molecules may be affected by temperature, pressure, and fluid composition, with the last two parameters having the greatest effect.

The addition of light, paraffinic components to an asphaltene-containing solution will lower the solubility power with respect to the asphaltenes. Resin molecules will react to the addition by desorbing from the asphaltenes in an attempt to reestablish thermodynamic equilibrium, thus increasing the probability of asphaltene self-aggregation.[6] An increase in the temperature generally affects the aggregation of asphaltenes by decreasing the solvating power of the crude oil,[7] but some controversy regarding the temperature effect exists in the literature. Several authors state that the asphaltene aggregate size decreases with increasing temperature (aromatic solvents).[8] Speight[5] states that the precipitation of asphaltenes increases with temperature. A

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precipitation maximum at 25 °C in paraffinic solvents has also been reported.[9]

Asphaltenes are also known to aggregate by pressure depletion alone.[6,10,11] By decreasing the pressure the relative volume fraction of the light components within the crude oil increases. This causes an increase in the solubility parameter difference between the crude oil and the asphaltenes, reaching a maximum at the bubble point pressure. Below the bubble point, asphaltenes are more soluble again due to evaporation of light crude oil components. The relative change in asphaltene solubility has been shown to be highest for light crude oils that are undersaturated with gas, and which usually contain only a small amount of asphaltenes.

The reversibility of the asphaltene aggregation is also a subject of some controversy in the literature. Hirschberg et al.[10] assumed that the aggregation was reversible, but probably very slow. Joshi et al.[12] found the precipitation from a live crude oil to be reversible in the matter of minutes, except for a subtle irreversibility observed for the first depressurization of the crude oil. They also discussed the different behavior of asphaltenes precipitated from crude oils with excess *n*-alkanes and by asphaltenes contained in the original crude oil. Hammami et al.[6] also found that the aggregation is generally reversible, but that the kinetics of the redissolution vary significantly depending on the physical state of the system.

The intention of this study is to explore the asphaltene aggregation by pressure depletion using NIR spectroscopy in combination with multivariate analysis techniques. Both a live crude oil and model systems of asphaltenes in toluene/pentane solvents have been studied in order to detect differences in asphaltene aggregation behavior. The crude oil studied is an undersaturated, low asphaltene (0.8 wt %) oil. From the de Boer plot, defining regions of expected asphaltene stability by correlating undersaturation versus in-situ density, this crude oil is classified as potentially creating slight asphaltene precipitation problems. In addition to the detection of asphaltene aggregation onset pressure, the reversibility of the aggregation is studied, both for the live crude oil and model systems. The recorded NIR spectra were subject to an on-line principal component analysis (PCA) routine, enabling instant and easy detection of any change in the aggregation state of the fluid.

Theory

Near-Infrared Spectroscopy. The near-infrared (NIR) spectroscopic region of the electromagnetic spectrum extends from 780 to 2500 nm (12820 to 4000 cm^{-1}), but the region generally used is between 1100 and 2500 nm (9090 to 4000 cm^{-1}). The NIR region is attractive for hydrocarbon analysis because many of the absorption bands observed in this region arise from overtones or combinations of carbon−hydrogen stretching vibrations. Functional groups such as methylenic, olefinic, or aromatic C−H give rise to various C−H stretching vibrations that are mainly independent of the rest of the molecule.[13] Asphaltenes, being large aromatic fusedring systems, also display $\pi\pi^*$ and nπ^* electronic transitions in the near-infrared region.

In addition to attenuation of the transmitted light by absorbance, light scattering by asphaltene aggregates in hydrocarbon solutions contributes to the light attenuation. For slightly lossy dielectric particles in the Rayleigh limit the light attenuation is a sum of the absorbance and scattering contribution

$$\sigma_{tot} = \sigma_{sc} + \sigma_{abs} \tag{1}$$

where σ_{tot}, σ_{sc}, and σ_{abs} are the total, scattering, and absorption cross-sections, respectively. The ratio of scattering to absorption scales with r^3 (radius of particle), indicating the importance of particle size on the total light attenuation. The influence of scattering increases extensively with increasing diameter of the particles, the particles being asphaltene aggregates in this case. The relation between optical density (OD), light intensity (I), number of particles (N) and particle cross section (σ_{tot}) is given as

$$OD = \log\left(\frac{I_0}{I}\right) = 0.434 N\sigma_{tot} \tag{2}$$

where I_0 and I are the intensities of incident and transmitted light, respectively. The measured optical density is thus a sum of the absorbance and the scattering contribution. The effect of multiple scattering is not accounted for in this equation. However, for the purposes of the present study a detailed description of the light scattering is not needed. The main objective is to distinguish samples of different asphaltene aggregation level based on the measured optical density (OD). Details on light scattering in the near-infrared region can be found in Mullins.[14]

Principal Component Analysis (PCA). The information contained in NIR spectra is embedded in multiple absorption bands. Often it is difficult to gain information from such spectra by univariate analysis techniques. However, by taking advantage of all the variables in the NIR spectra by multivariate analysis much useful information can normally be extracted. One particularly efficient technique for analyzing NIR data is principal component analysis (PCA). PCA is a projection method that helps visualize the most important information contained in a data set by combining variables that describe major trends in the data.

Mathematically, PCA is based on an eigenvector decomposition of the covariance matrix of the variables in a data set. Given a data matrix **X** with *m* rows of samples and *n* columns of variables, the covariance matrix of **X** is defined as

$$\{\text{cov}\}(\mathbf{X}) = \frac{\mathbf{X}^T\mathbf{X}}{m-1} \tag{3}$$

The result of the PCA procedure is a decomposition of

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(11) de Boer, R. B.; Leerloyer, K.; Eigner, M. R. P.; van Bergen, A. R. D. *Screening of Crude Oils for Asphalt Precipitation: Theory, Practice, and the Selection of Inhibitors*; Cannes, 1992; pp 259−270.

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Table 1. Composition of Recombined Crude Oil

component	mol %
N_2	0.6
CO_2	2.0
C1	33.3
C2	6.5
C3	7.5
iC4	1.2
nC4	4.4
iC5	1.5
nC5	2.4
C6	3.0
C7	4.5
C8	4.4
C9	3.1
C10+	25.7

the data matrix **X** into principal components called score and loading vectors

$$\mathbf{X}_{n\times m} = \mathbf{t}_1\mathbf{p}_1^T + \mathbf{t}_2\mathbf{p}_2^T + \mathbf{t}_i\mathbf{p}_i^T + ... + \mathbf{t}_k\mathbf{p}_k^T + \mathbf{E}_{n\times m} \quad (4)$$

Here $\mathbf{t}_i$ is the score vector, $\mathbf{p}_i$ is the loading vector, and **E** is the residual matrix. The score and loading vectors contain information on how the samples and variables, respectively, relate to each other. The direction of the first principal component ($\mathbf{t}_1$, $\mathbf{p}_1$) is the line in the variable space that best describes the variation in the data matrix **X**. The direction of the second principal component is given by the straight line that best describes the variation not described by the first principal component and so on. Thus, the original data set can be adequately described using a few orthogonal principal components instead of the original variables, with no significant loss of information. When plotting principal components against each other in so-called score plots, relations between samples are easily detected.[15] In this study PCA is shown to be a very efficient tool in separating the effects of fluid compressibility and asphaltene aggregation on NIR spectra.

Experimental Section

Both depressurization of a live crude oil and model systems of asphaltenes in toluene/*n*-pentane solvents were studied with respect to asphaltene aggregation. The live oil was prepared by recombining a dead oil sample with natural gas in a recombining cell to the original reservoir bubble point condition of 155 bar at 125 °C. The composition of the crude oil is given in Table 1. The recombined crude oil was left to equilibrate for 14 days at 300 bar with continuous mixing.

The model systems were prepared from asphaltenes precipitated from a crude oil in excess *n*-pentane (1:10). After precipitation and 24 h to equilibrate, the asphaltenes were obtained by filtering the solution through a 0.45 μm filter (Millipore) and dried. The dried asphaltenes were then dissolved in toluene.

It was of importance that the asphaltene model systems used for the depressurization study were in a state close to precipitation conditions. To find such systems a titration study under atmospheric conditions was conducted by titrating a 2.0 wt % asphaltene-in-toluene solution with *n*-pentane. The onset of asphaltene aggregation was detected with a NIR spectrometer (Brimrose AOTF Luminar 2000) equipped with a fiber optic sampling probe for transflectance measurements. In Figure 1 the optical density at 1600 nm as a function of added pentane is shown. In the first part the optical density decreases as a consequence of dilution of the asphaltene solution. At

(15) Wise, B. M.; Gallagher, N. B. *J. Proc. Cont.* **1996**, *6*, 329–348.
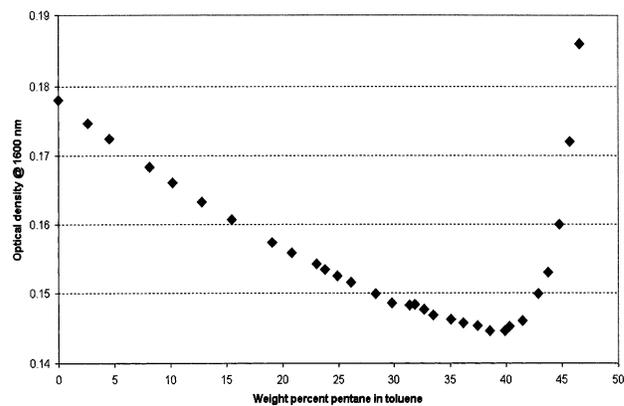
Figure 1. Optical density as a function of added *n*-pentane to a 2.0 wt % asphaltene-in-toluene solution. Aggregation onset approximately at 40 wt % added pentane.
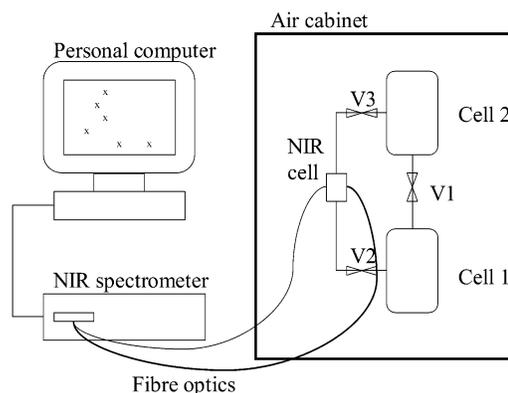
Figure 2. High pressure near-infrared system. Spectrometer connected to high-pressure NIR cell through fiber optics. Maximum operating conditions: 325 bar and 200 °C.

Table 2. Composition of Model Systems

	35 wt % pentane	40 wt % pentane	40 wt % pentane, no asphaltenes
n-pentane [wt %]	34.6	39.5	40
toluene [wt %]	64.2	59.3	60
asphaltenes [wt %]	1.2	1.2	
	100	100	100

around 40 wt % pentane the optical density starts to increase due to the formation of larger asphaltene aggregates. This was then defined as the asphaltene aggregation onset point for the model system.

Based on the results shown in Figure 1 two model solutions of pentane and toluene were made, one at 35 wt % pentane, the other at 40 wt % pentane. The pentane content was chosen such as to be sure that no asphaltene aggregation would take place at atmospheric conditions. Model asphaltene systems were made by adding 1.2 wt % asphaltenes to the pentane/toluene solutions, corresponding approximately to the dilution of the original 2.0 wt % asphaltene-in-toluene solution with 35 and 40 wt % pentane. The composition of the model systems along with a system containing no asphaltenes is given in Table 2. Samples of 500 mL of the model systems were transferred to high-pressure sample bottles and mechanically pressurized to 300 bar.

A modified PVT rig (ROP HDV160) was used for the asphaltene aggregation study. The rig consisted of two connected 80 cm³ cells with a maximum operating pressure of 1000 bar. The cells were mounted in an air bath of constant temperature (max 200 °C). The system is depicted schematically in Figure 2. The cells were connected through valve V1, but this valve could be bypassed through valves V2 and V3.
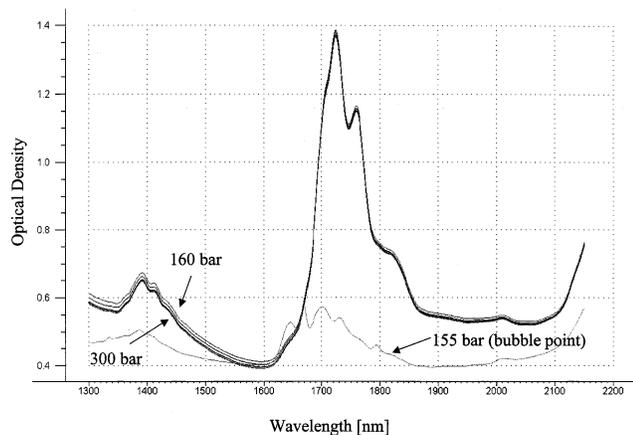
Figure 3. NIR spectra obtained during pressure depletion of crude oil from 300 to 150 bar.

For the asphaltene aggregation study a high-pressure, high-temperature transmission NIR cell (Equitech) was mounted between the cells. The NIR cell had a maximum operating pressure of 325 bar, and an optical path length of 1.5 mm. The NIR cell was connected to the Brimrose spectrometer outside the climatic air cabinet through fiber optics. The spectrometer was fast, making it possible to display spectral scans from 1100 to 2200 nm on the personal computer in a few seconds. Alternatively the spectra could be displayed as points in a score plot as will be described.

Both the live crude oil and the model systems were transferred to the PVT rig at 300 bar. The two high-pressure cells were filled with 40 mL of sample each, a total of 80 mL. Five depressurization runs were performed, all at isothermal conditions. The live oil was depressurized at the reservoir temperature of 125 °C. The 35 wt % pentane model system was depressurized at both 100 °C and 150 °C, while the 40 wt % pentane model system was depressurized at 100 °C. In addition, a run with the 40 wt % pentane solution without asphaltenes was performed at 150 °C. The crude oil and the 35 wt % pentane solution at 150 °C were also repressurized in order to gain information on the reversibility of the asphaltene aggregation. The model system temperatures (100 °C and 150 °C) were chosen to be in the same range as the temperature used for the recombined crude oil (reservoir temperature, 125 °C).

The samples were depressurized from 300 bar in discrete steps, starting at intervals of 20 or 40 bar. The pressure intervals were reduced at lower pressures. For each step 30 cm³ of sample material was passed through the NIR cell (valve V1 closed) from the upper to the lower cell, and then up again. After 5 additional minutes to equilibrate, four spectra were taken with 30 s intervals. Including the time used in passing the sample through the cell the samples were by this procedure held for a total of 20 min at each pressure level before scanning. After scanning the pressure was reduced again, and the sampling routine was repeated. The NIR spectra were analyzed by a LabVIEW[16] PCA routine. The results were successively plotted in a score plot of the first and second principal component. The PCA routine visualized even small spectral changes during the depressurization run.

Results and Discussion

Onset of Asphaltene Aggregation. *Live Crude Oil.* Figure 3 shows the NIR spectra from 1300 to 2150 nm for the live crude oil depressurization from 300 to 150 bar. This wavelength section is chosen to avoid nonlinear effects in both ends of the scanned wavelengths from 1100 to 2200 nm. The spectra are dominated by the CH absorption peaks at approximately 1400 and 1725 nm. The spectral elevation with depressurization is also clearly seen, especially at lower wavelengths. This spectral elevation, hereafter called baseline elevation, is a general increase in optical density for all wavelengths due to light scattering.

As soon as the pressure was reduced to the bubble point at 155 bar gas started to evolve inside the NIR cell. The spectra at 155 and 150 bar are seen to be very different from the pure liquid spectra, with much lower absorption. These two spectra are almost identical and cannot be distinguished from each other in the figure. At 150 bar spectra of the pure liquid phase after gas evolution were recorded in addition to the bubble point spectra at the same pressure.

It is not easy to directly determine an asphaltene aggregation onset pressure from the baseline elevation of the NIR spectra in Figure 3. The differences in optical density are quite small, and the interpretation of the spectra is further complicated by the effect of fluid compressibility. In wavelength regions with low absorption the baseline elevation at low pressures due to light scattering dominates. For instance, around 1600 nm hydrocarbon absorption of NIR light is negligible and the measured optical density is mostly caused by light scattering. This means that in this area the optical density is highest for the spectra at low pressures, containing the largest asphaltene aggregates. In wavelength regions of high absorption, however, the higher density of the fluid at high pressures produces high values of optical density. One such region is the absorption peak at 1725 nm. At this wavelength both the baseline elevation effect and the compressibility effect influence the optical density. At 1725 nm the highest optical density value is displayed by the measurement of the oil phase at 150 bar due to heavy asphaltene aggregation. The second highest value of optical density is displayed by the spectrum at 300 bar due to the compressed state of the fluid at this high pressure.

Principal component analysis (PCA) is a powerful tool to distinguish the different effects seen in the NIR spectra, and at the same time keep all the information contained in the spectra by using a large number of wavelengths. A PCA model was built for the spectra of the crude oil in Figure 3 using the wavelengths from 1300 to 2150 nm as variables. The spectra below the bubble point were left out of the analysis, but the liquid-phase spectrum at 150 bar was included. Unscrambler 7.6[17] was used for the modeling, and no pretreatment of the spectra was performed. The resulting score plot for the live crude oil depressurization is shown in Figure 4.

Starting from the high-pressure condition the system is seen to follow a more or less linear trend along principal component 2 (PC2). Reaching lower pressures the scores are located along PC1 as a function of depressurization. The turning point is found around 180 bar. PC1 contains most of the spectral variance, explaining 93.8% of the data. PC2 explains 5.9% of the variance. High variance for a principal component means that it describes a large part of the differences between the NIR spectra.

(16) National Instruments, *LabVIEW6*; 2000.

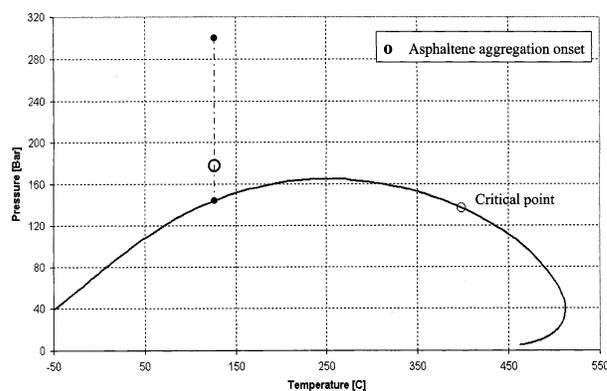(17) CAMO ASA, *The Unscrambler v7.6*; 2000.
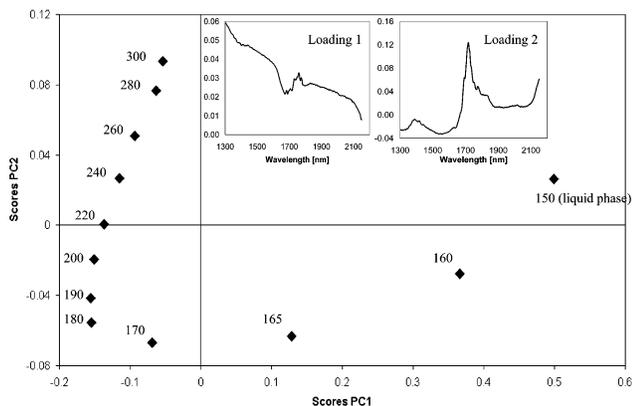
Figure 4. Score plot of depressurization of crude oil. PC1: 93.8%, PC2: 5.9%. Aggregation onset approximately at 180 bar. First and second loading vector included.

The information contained in the principal components may be interpreted by studying the corresponding loading vectors. The loadings of score vectors 1 and 2, respectively, for the crude oil are also shown in Figure 4. The loading vectors show the parts of the NIR spectra that dominate the corresponding score vectors. The first loading vector illustrates a general baseline elevation effect, with the baseline elevation being largest for the lowest wavelengths. Such a baseline elevation is caused by scattering of the NIR light, believed to be caused by growing asphaltene aggregates in this case. This assumption will be further verified later when discussing the model systems. Loading vector 2 is dominated by absorbance in the band around 1725 nm. This corresponds to the CH absorption band seen in Figure 3. Samples with high score values along PC2 thus have higher absorption peaks. This is explained by the fluid compressibility, giving rise to more absorption at high pressures. The high-pressure samples thus have high scores along PC2.

The decomposition of the spectral information by PCA in Figure 4 is seen to be a very efficient tool to distinguish the aggregation effect from the pressure effect (compressibility). The turning point seen in the score plot at 180 bar can be defined as the onset of asphaltene aggregation, and the aggregation is seen to increase rapidly from 180 to 150 bar. The compressibility effect from 180 to 300 bar is much less pronounced, since PC2 only accounts for 5.9% of the spectral variance. Also, from the loading vector of PC2 in Figure 4 it is seen that the effect of fluid compressibility on the spectra is low in the region around 1600 nm. This confirms that the optical density change in this region is caused by light scattering, not absorption.

In Figure 5 the phase envelope of the crude oil as predicted by PVTsim[18] is shown. The pressure depletion path and the experimental asphaltene aggregation onset point are indicated. At 125 °C a bubblepoint of 145 bar is predicted, which is quite consistent with the observed bubble point of 155 bar.

It has been established that for high pressure, NIR spectra are linear in density of the sample (in absence of scattering).[12,19] This can also be seen by the straight-line portion in the score plot from 300 to 200 bar. The

(18) Calsep A/S. *PVTsim*; v11.0 ed.; 2001.
(19) Mullins, O. C.; Joshi, N. B.; Groenzin, H.; Daigle, T.; Crowell, C.; Joseph, M. T.; Jamaluddin, A. *Appl. Spectrosc.* **2000**, *54*, 624629.

Figure 5. Phase envelope of the crude oil with aggregation onset, depletion path, and critical point indicated.
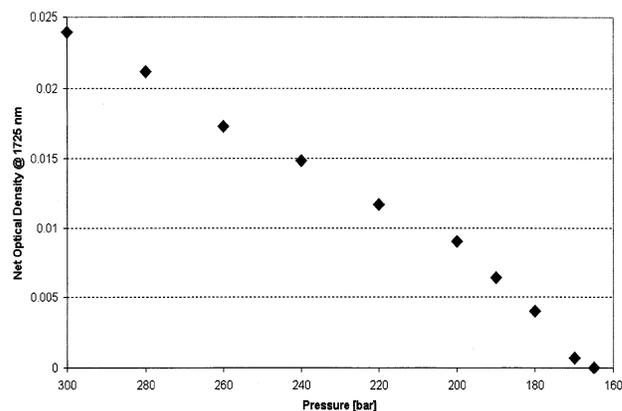
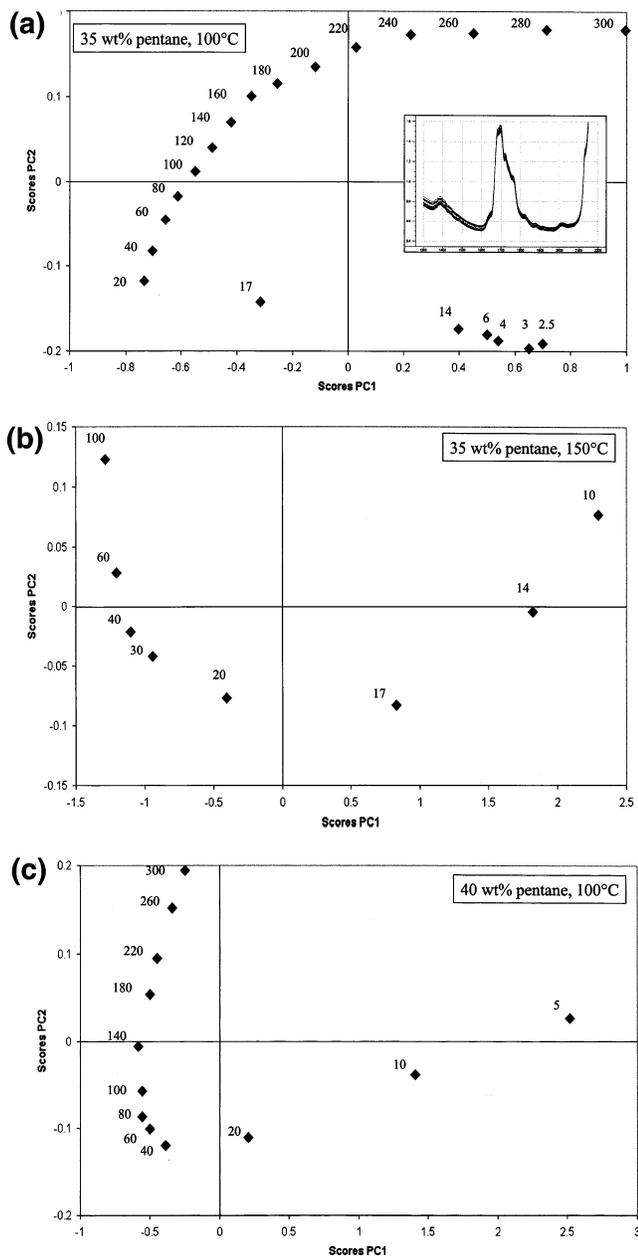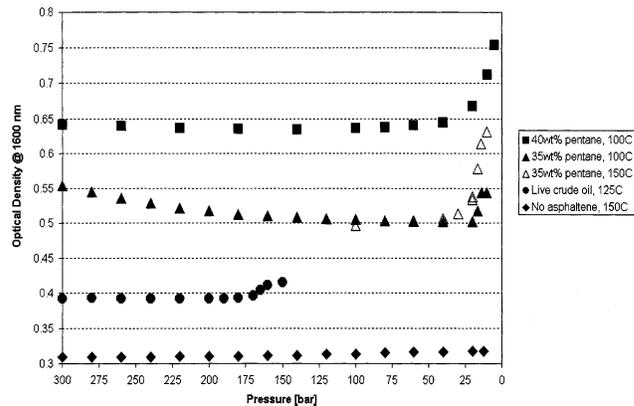**Figure 6.** Baseline corrected optical density for the NIR spectra of the crude oil at 1725 nm versus pressure. $R^2 = 0.99$.

linear pressure dependence can also be demonstrated for a single wavelength, for instance the peak at 1725 nm. In Figure 6 the net optical density from 300 to 165 bar is shown. The optical density values are baseline corrected in order to remove the effect of light scattering at lower pressures. This is done by subtracting the 300 bar spectrum from all spectra. The baseline corrected curve has a R^2 value of 0.99 when fitted to a straight line, confirming the linearity in mass density for NIR spectra at high pressures. By baseline correcting the spectra the effect of aggregation is more or less removed and the compressibility effect can be isolated even if the original spectra are influenced by the light scattering.

Model Systems. Inside Figure 7a the NIR spectra from 300 to 2.5 bar for the 1.2 wt % asphaltene model system in the 35/65 wt % toluene/pentane solution (100 °C) are shown. The pressure dependence resembles the live crude oil spectra, and the increase in absorption from 1600 to 1300 nm due to the asphaltene content is clearly seen. The same PCA modeling was performed as for the live crude oil. The corresponding score plots for all three model systems are given in Figure 7a–c. The score plots resemble the score plot of the live crude oil, with an exception for the high-pressure samples of the 35 wt % pentane model system at 100 °C in Figure 7a. A distinct baseline decrease is seen from 300 to approximately 200 bar before the normal behavior displayed by the other systems then is followed down to 2.5 bar. The reason for this unexpected baseline decrease is not clear, but some kind on nonequilibrium in the system when the measurements are started could be a possible explanation.

Figure 8. Optical density at 1600 nm versus pressure for all five systems. No effect of aggregation seen for the asphaltene-free system.
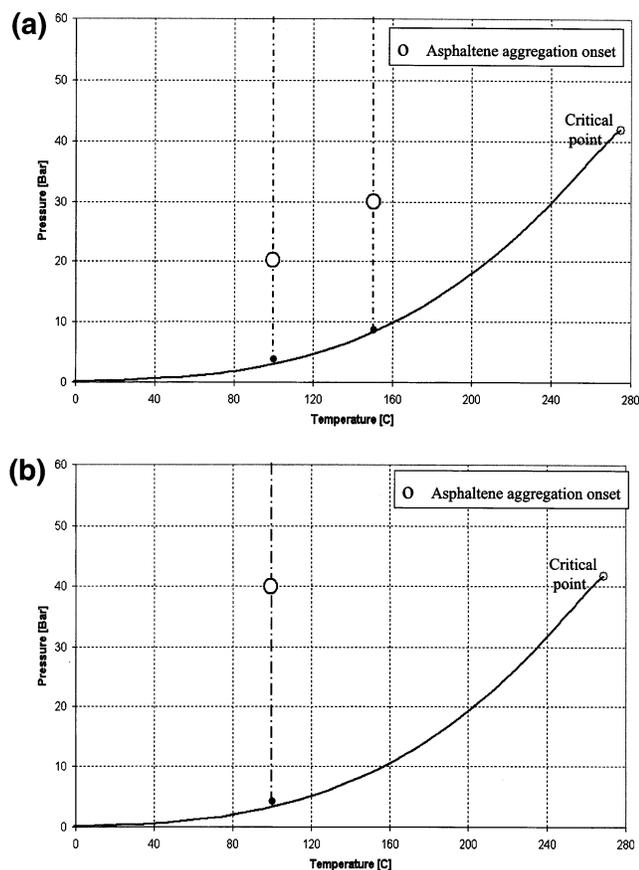
Table 3. Bubble Points and Asphaltene Aggregation Onset Pressures

system	temperature [°C]	bubblepoint [bar]	onset pressure [bar]
crude oil	125	155	180
35 wt % pentane	100	<2.5	20
35 wt % pentane	150	10	30
40 wt % pentane	100	<2.5	40
40 wt % pentane, no asphaltene	150	14	-

model systems due to its higher bubble point is evident. In addition the amount of asphaltene aggregation is clearly less for the live crude oil than for the model systems, as seen from the smaller increase in optical density. For the 35 wt % pentane model system, the aggregation starts at a higher pressure for the 150 °C experiment than the one at 100 °C. The amount of aggregation is also higher for the high-temperature case, which could be explained by the fact that the last measurements in the high-temperature case are close to the bubble point at 10 bar. The amount of aggregation will be at its maximum at this bubble point pressure. For the model systems at 100 °C no bubble point could be detected even at the lowest recorded pressure, 2.5 bar. For the 40 wt % pentane solvent the asphaltene aggregation onset point is also markedly higher than for the 35 wt % solvent at the same temperature (100 °C).

From Figure 7a−c an approximate asphaltene aggregation onset pressure can be found for all three model systems. These pressures are given in Table 3, along with the detected bubble point pressures. Data for the live crude oil and the asphaltene-free model system are also included. It should also be noted that the appearance of the score plots are more or less the same, regardless of the type of system studied, a live crude oil or a model system of pentane/toluene/asphaltene.

In Figure 9a and b the bubble point curves of the 35 wt % and 40 wt % pentane model systems are shown. The curves are calculated by PVTsim[18] without including the asphaltene fraction. This heavy fraction will however not influence the bubble point curves. The lower part of the pressure depletion path and the experimental asphaltene aggregation onset points are indicated. In Figure 9a an increase in onset pressure with temperature is seen.

Figure 7. (a) Score plot of depressurization of 35 wt % pentane model system at 100 °C. PC1: 93.6%, PC2: 6.2%. Aggregation onset approximately at 20 bar. NIR spectra included. (b) Score plot of depressurization of 35 wt % pentane model system at 150 °C. PC1: 99.7%, PC2: 0.2%. Aggregation onset approximately at 30 bar. (c) Score plot of depressurization of 40 wt % pentane model system at 100 °C. PC1: 98.6%, PC2: 1.2%. Aggregation onset approximately at 40 bar.

To further verify the asphaltene aggregation effect, a depressurization of a toluene/pentane system without asphaltenes was performed. The optical density at 1600 nm as a function of pressure for this system is plotted with the other systems in Figure 8. Indeed, no baseline elevation with depressurization is seen for this system, as opposed to the asphaltene-containing systems. In addition, the negligible amount of absorption even at high pressures at this wavelength is demonstrated, confirming that changes in optical density at 1600 nm is caused by light scattering effects.

From Figure 8 the higher asphaltene aggregation onset point for the live crude oil as compared to the

Figure 9. (a) Bubble point curve for the 35 wt % pentane model system with aggregation onsets, lower part of depletion paths, and critical point indicated. (b) Bubble point curve for the 40 wt % pentane model system with aggregation onset, lower part of depletion path, and critical point indicated.

Reversibility of Asphaltene Aggregation. The redissolution of the asphaltene aggregates by repressurizing was studied for two of the systems, namely, the live crude oil and the 35 wt % pentane model system at 150 °C. The live crude oil was repressurized in steps to 300 bar, while the model system was repressurized to 100 bar. The NIR sampling during repressurization followed the same procedure as described earlier for the depressurization. At the maximum pressure NIR spectra were recorded in intervals for several hours. However, the same amount of sample material was passed between the cells, and the same time was allowed to equilibrate before each NIR scan as for the depressurization/repressurization cycles. This was done to ensure equal sampling conditions for all measurements.

A new PCA model was built, combining the depressurization and repressurization NIR spectra. The results for the live crude oil are given in Figure 10a. Considerably redissolution of asphaltenes by increasing the pressure to 160 and 170 bar is seen due to the movement along PC1. By further increase of the pressure the compressibility effect along PC2 dominates. The samples follow more or less the same trend as seen for the high-pressure depressurization when increasing the pressure from 180 to 300 bar, but with a shift along PC1 indicating larger aggregates. This indicates that after the initial repressurization from 150 to 170 bar no significant redissolution is taking place within the time frame of the experiment. When reaching 300 bar,
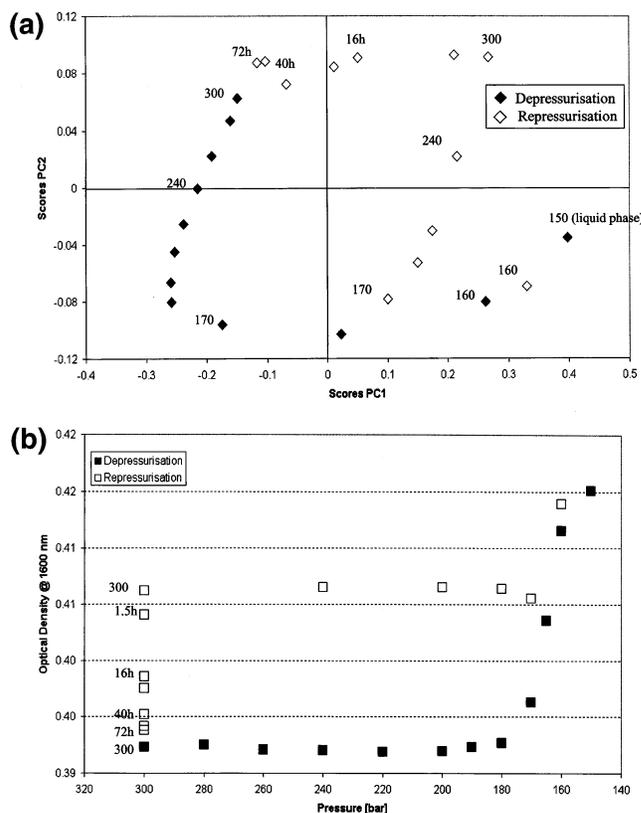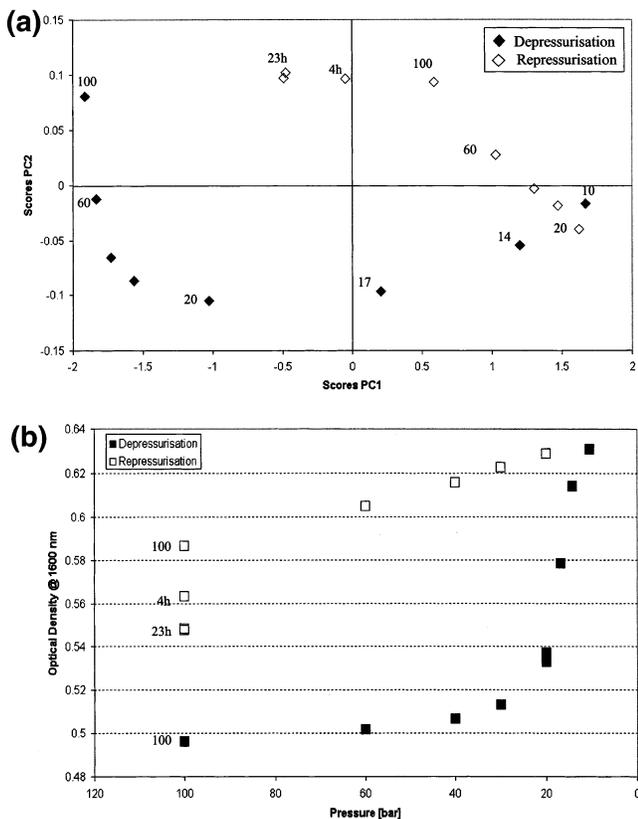

Figure 10. (a) Score plot of the depressurization/repressurization of the crude oil. PC1: 89.4%, PC2: 10.2%. A time of 72 h to equilibrate was allowed after repressurization to 300 bar. (b) Optical density at 1600 nm versus pressure for the depressurization/repressurization of the crude oil.

repeated measurements at this pressure were taken. This is in Figure 10a indicated by the number of hours allowed to equilibrate at this pressure. It is seen from the figure that the asphaltene aggregation indeed is reversible, but clearly time-dependent. The samples at 300 bar moves along PC1, indicating aggregation dissolution, and approaches the initial measurement at 300 bar. The last measurements after 65 and 72 h are slightly offset along the PC2 axis, but there is no major spectral difference between these measurements and the first at 300 bar since PC2 for this model only accounts for 10.2% of the total variation, as compared to 89.4% by PC1. The redissolution is seen to be a hysteresis process, approaching the initial state if enough time to equilibrate is allowed.

To better isolate only the aggregation effect, the optical density may again be plotted as a function of only one wavelength, 1600 nm, instead of all wavelengths, as for the PCA method. Figure 10b shows the optical density at 1600 nm for the live crude oil plotted as a function of the pressure. Again the initial redissolution when repressurizing to 170 bar is clearly seen, along with the hysteresis effect made up by the lack of further redissolution during repressurization. When time is allowed to equilibrate at 300 bar the initial optical density is approached, and at 72 h the optical density at 1600 nm is close to the initial measurement at 300 bar.

Figure 11a shows the same score plot as for the live crude oil in Figure 10a for the 35 wt % pentane model system at 150 °C. More or less the same trends as for

Figure 11. (a) Score plot of the depressurization/repressurization of the 35 wt % pentane model system at 150 °C. PC1: 99.5%, PC2: 0.3%. A time of 23 h to equilibrate was allowed after repressurization to 100 bar. (b) Optical density at 1600 nm versus pressure for the depressurization/repressurization of the 35 wt % pentane model system at 150 °C.

the live crude oil can be identified for the model system. However, some redissolution seems to take place during repressurization to 100 bar due to the movement along PC1 from 20 to 100 bar seen in the score plot. In addition it seems like the redissolution stops at an earlier stage than for the live crude oil. These effects are also seen in the plot at 1600 nm in Figure 11b.

It seems like while the aggregation of asphaltenes in the live crude oil is a more or less reversible process, the aggregation in the model system is only partially reversible. No further redissolution of the aggregates was seen from 20 to 23 h of equilibration. However, the possibility that the aggregation of the model system asphaltenes is reversible if even more time is allowed for equilibration cannot be excluded.

The asphaltenes used in the model system have been precipitated by excess *n*-pentane when being prepared. These asphaltenes might be very different from the asphaltenes contained in the live crude oil, which have not been subject to any pretreatment. This difference between "field asphaltenes" and "lab asphaltenes" has been discussed by Joshi et al.[12] Initially asphaltenes present in a crude oil are stabilized by resin molecules, preventing any major aggregation of the asphaltenes. During depressurization of a crude oil the increase in molar volume of the light components is larger than for the heavier components. Since the relative volume of the components having the poorest asphaltene solubility power increases, the amount of asphaltene aggregation correspondingly increases. By repressurizing the com-

pressible crude oil the asphaltene aggregates redissolve more or less completely. This behavior is confirmed in this study by the nearly complete redissolution of the aggregates. On the other hand, when preparing the asphaltenes for the model system (lab asphaltenes) the asphaltenes will be stripped for the resins, since this fraction is soluble in the added pentane. This resin-free asphaltene fraction will not be able to regain its initial state of aggregation when aggregates once have formed. This thought is also supported by the behavior of the repressurized model system in this study, where only a partial reversibility of the aggregation is observed.

The redissolution kinetics of the aggregated asphaltenes has been shown to be relatively slow. This might suggest that more time should have been allowed for equilibration at each pressure level during the aggregation onset detection procedure. For a more detailed study shorter pressure intervals, especially in the vicinity of the onset pressure, could have been utilized. The PCA routine is able to detect even small changes in the spectral features, and using the on-line PCA routine it is easy to detect the onset pressure with great accuracy if desirable.

Conclusions

The detection of bubble points and asphaltene aggregation onset pressures by near-infrared spectroscopy for both a live crude oil and model systems has been demonstrated. The aggregation onset pressure is seen as a baseline elevation of the NIR spectra due to light scattering. The similar behavior of the crude oil and the asphaltene containing model systems confirms the assumption that the baseline elevation is caused by growing asphaltene aggregates. Also, asphaltene-free model systems show no baseline elevation of the NIR spectra with pressure depletion. By use of principal component analysis (PCA) the effect of asphaltene aggregation is easily distinguished from the effect of fluid compressibility, an effect which also influences the high-pressure NIR spectra.

The asphaltene aggregation from a live crude oil has been shown to be more or less completely reversible, although 72 h of equilibration was needed to completely redissolve the asphaltene aggregates. The results also indicated that the redissolution of asphaltene aggregates formed by pressure depletion of model asphaltene systems was only partially reversible. This was explained by the stripping of the resin fraction when preparing asphaltenes for the model systems.

The use of high-pressure near-infrared spectroscopy in combination with multivariate analytical techniques such as PCA has been shown to be an efficient tool in studying the aggregation state of asphaltene-containing systems. The combination of NIR with PCA produces a very sensitive procedure for aggregation onset detection. The robustness of the high-pressure NIR cell allows operation in a wide range of pressures and temperatures, and since the NIR technique is noninvasive the sample is not altered in any way. This makes the technique very suitable for investigations of live crude oil samples from high-pressure reservoirs.

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