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ORIGINAL CONTRIBUTION

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Near-IR study on the dispersive effects of amphiphiles and naphthenic acids on asphaltenes in model heptane-toluene mixtures

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Abstract Near-IR spectroscopy is used to follow the disintegration of asphaltene aggregates at 1,600 nm. It is shown that the technique is applicable to determine the efficiency of various additives as disaggregation chemicals.

Keywords Asphaltenes · Naphthenic acids · Near-IR spectroscopy · Inhibitors

Introduction

Asphaltenes are defined by solubility characteristics: they are insoluble in light alkanes such as *n*-heptane and are soluble in toluene [1]. They are generally composed of polyaromatic nuclei carrying aliphatic chains and rings and a number of heteroatoms, including sulphur, oxygen, nitrogen and metals such as vanadium, nickel and iron. These heteroelements account for a variety of polar groups, such as aldehyde, carbonyl, carboxylic acid, amine and amide [2, 3, 4]. As one of the primary components of crude oil, asphaltenes are known to cause a number of problems in connection with production, transport and processing of crude oils [5, 6, 7, 8]. The state of the asphaltenes is dependent upon pressure and temperature as well as the composition of the crude oil [9, 10, 11, 12, 13, 14]. It is probable that they will precipitate and cause plugging of reservoirs or production equipment if they are exposed to large changes in these parameters. The general view is that at high pressures, the asphaltenes are in a condition of monomeric entities dissolved in the crude oil. At lower pressures, the asphaltenes exists as aggregates (micelles) [15, 16] of entities with an altogether elliptical form [17]. These aggregates are kept dispersed in the solution by resins [18, 19, 20, 21, 22], which are molecules similar to the asphaltenes containing various polar groups as the asphaltenes do, yet are soluble in light alkanes and insoluble in toluene.

Gonzalez and Middea [23] studied the peptization of asphaltenes in aliphatic solvents by various oil-soluble amphiphiles. They showed that the effectiveness of amphiphiles on asphaltene stabilization was influenced by the interactions between the polar headgroups of the amphiphiles and polar groups on the asphaltene molecules; however, their results also indicated that other interactions could be of importance, for instance, the π electrons of the aromatic portions of the asphaltenes may act as electron donors for hydrogen bonds with hydroxyl groups of the amphiphiles. In 1994, Chang and Fogler [24, 25] discussed the stabilization of asphaltenes in aliphatic solvents using alkylbenzene-derived amphiphiles. The results supported earlier suggestions of a hydrogen-bonding effect or possible acid–base interactions between the amphiphile headgroups and polar groups on the asphaltenes, and also showed that the length of the amphiphiles alkyl tail was of significance.

In this study the disintegration of asphaltene aggregates is studied by means of near-IR (NIR) spectroscopy. The NIR technique is introduced as a powerful tool for screening the efficiency of chemicals for this purpose.

Experimental

Preparation of asphaltenes

The asphaltenes were precipitated from a North Sea crude oil by gently mixing crude oil and *n*-heptane (1:20 gml^{-1}) at room temperature for 12 h without exposure to light. The mixture was then filtrated through a microfilter (pore diameter 0.45 μm) to separate the asphaltenes from the diluted crude oil. The filtrate was then washed in *n*-heptane with constant stirring for 1 h before being filtrated and dried under a N_2 atmosphere to constant weight.

Preparation of asphaltene stock solution

The dried asphaltenes were dissolved in toluene before *n*-heptane was added. The stock solution then consisted of 0.25 wt% asphaltenes in a mixture of *n*-heptane and toluene with a ratio of 70/30 v/v. The stock solution was allowed to equilibrate with constant stirring for 48 h before the measurements started.

Preparation of samples with additives

The additives were dissolved in *n*-heptane/toluene, or in some cases where this was difficult, they were first dissolved in toluene and then the *n*-heptane was added. The solutions with additives were then mixed with an equal amount by weight of asphaltene stock solution, before the NIR measurements started. Each sample was then made up of 0.125 wt% asphaltenes in 70/30 *n*-heptane/toluene with various concentrations of additives. Spectra were taken every minute (Fig. 1) with constant mixing throughout the experiment. The first spectrum in each series was set as a background and subtracted from the rest of the spectra. Since the asphaltenes were partly precipitated in the *n*-heptane/toluene mixture, it was crucial with constant stirring to ensure a homogeneous mixture during the NIR measurements. The physical properties of the chemical additives and solvents are summarized in Table 1.

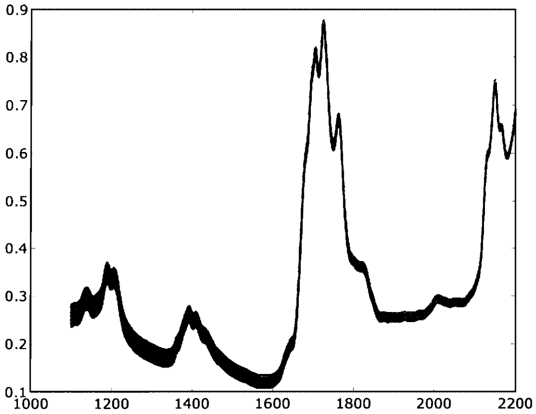


Fig. 1. Near-IR (*NIR*) spectra of 0.125 wt% asphaltenes in a 70/30 *n*-heptane/toluene mixture with 1.25 wt% inhibitor A added. A total of 1,200 spectra were measured and the time between each spectrum was 1 min

NIR sampling

The NIR measurements were performed with a Brimrose AOTF Luminar 2000 spectrometer equipped with a fiber optic sampling probe for transflectance measurements. The wavelength region was set to 1,100–2,200 nm, and the total number of scans per spectrum to 32. The total path length was 1 mm, and the experiments were performed at room temperature (22 °C). In the comparison of the effectiveness of the additives, we utilized the results from 1,600 nm. The reason for this choice is that hydrocarbon absorption is minimal in this region, and that this is the NIR region with the least noise in the measurements.

Theory

Light scattering by asphaltene aggregates in the NIR region

The general theory behind optical scattering and absorption is a well-explored field and is described in detail in the literature [26]. In this work, our interest centers on the light extinction in the IRspectral range, which can be accounted for by two distinct mechanisms: electronic absorption by organic molecules and scattering from particles or aggregates. The absorption spectra in the NIR range from 780 to 2,500 nm (12,820 to 4,000 cm^{-1}) consist of overtones and combinations of the fundamental molecular vibration bands, which are primarily due to hydrogenic stretches of C–H, N–H, S–H and O–H bonds. In crude oils, the scattering depends strongly upon the shapes and sizes of asphaltene, wax and hydrate particles. A common way to create light spectra is to measure the relative amount of light transmitted through a solution and to convert the measured transmittance, *T*, into optical density (OD) by nonlinear transformation. The OD of the sample expresses the amount of light that has been lost in the sample and is linearly related to the total cross section by

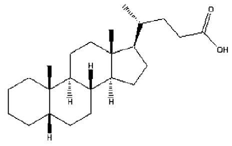
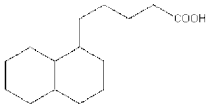
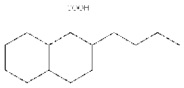
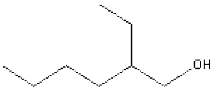
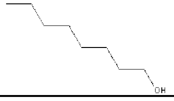
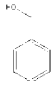
$$\mathrm{OD} = \log(I_0/I) = 0.434N\sigma_{\mathrm{tot}}, \tag{1}$$

where I_0 and I are the intensities of incident and transmitted light and N is the number of particles in the total cross section σ_{tot}. For slightly lossy dielectric spheres, electronic absorption, σ_{abs}, and optical scattering, σ_{sca}, contribute separately to the light extinction.

$$\sigma_{\mathrm{tot}} = \sigma_{\mathrm{sca}} + \sigma_{\mathrm{abs}} \tag{2}$$

The scattering can be divided into two groups: wavelength-independent scattering, where the size of the scatterer is very large compared to the wavelength of the light, and wavelength-dependent scattering, where the particles are of comparable sizes to or smaller than

Table 1. A summary of the amphiphiles and naphthenic acids used as additives in this study

Name	Molecular weight	Chemical structure	Source	Purity (wt%)
5-β(H)-cholanoic acid [CHOL]	361		Chiron AS	> 95
1-Naphthalenepentanoic acid, decahydro [2C4]	238	 I	Chiron AS	> 90
1-Naphthalenoic acid, decahydro-2-buthyl [C42]	238	 II	Chiron AS	> 90
Crude naphthenic acid [CNA]	250	Mixture	Corn van der Locke	-
Fluka naphthenic acid [Fluka]	240	Mixture	Fluka	-
Naphthenic acid from North Sea [North Sea]	400	Mixture	Extracted	-
2-Ethyl-1-hexanol	130.23		Merck	> 99
1-Octanol	130.23		Merck	> 99
Benzyl alcohol	108.14		Fluka	> 98
Hexylamine	101.94		Merck	> 98
n-Alkylbenzenesulfonic acid, (n = C_{10}-C_{13}) [ABSA]	385.5		Alfa Aesar	96+
Inhibitor A	-	Mixture	Tros / Dyno	-

[a] Up to 30 wt% unsaturated bonds in cyclic part of molecular structure
[b] Up to 10 wt% unsaturated bonds in cyclic part of molecular structure

the wavelength of the light. The latter group contains the case of $r/\lambda \leq 0.05$ (the Rayleigh condition), where λ is the wavelength of light and r the particle radius. Then, the scattering is purely dipolar with high-order scattering moments vanishing, and σ_{sca} is given by

$$\sigma_{\mathrm{sca}} = \frac{8\pi}{3} k^4 r^6 \left(\frac{\varepsilon - 1}{\varepsilon + 2} \right)^2 , \tag{3}$$

where ϵ is the dielectric constant and $k = 2\pi/\lambda$. σ_{abs} can be represented as

$$\sigma_{\mathrm{abs}} = 12\pi k r^3 \left(\frac{\varepsilon''}{(\varepsilon' + 2)^2 + \varepsilon''^2} \right), \tag{4}$$

where ϵ' and ϵ'' are the real and imaginary parts of the dielectric constant, respectively. The ratio of scattering to absorption cross-sections scales with r^3; hence, for a given value of ϵ'', the particle size is very important for determining the magnitude of the particle scattering. This produces the result that, under the assumption of no multiple scattering, a larger number of smaller spheres are less efficient scatterers than a smaller number of larger spheres, for a given mass of material.

For particles approaching the wavelength of light, the scattering is still dependent on the wavelength, but with a power less than 4. Heller [27] used the Stevenson [28, 29] extension of the Rayleigh equation to develop a relation for sizes just larger than Rayleigh scatterers. Here the wavelength exponent, g, i.e. the power of r/λ in the scattering efficiency, can be represented in closed form by

$$g = 4 + \frac{12(n^2 - 2)\alpha^2}{5(n^2 + 2) + 6(n^2 - 2)\alpha^2}, \tag{5}$$

where

$$\alpha = \frac{2\pi r n}{\lambda}, \quad \alpha \leq 1 \tag{6}$$

and n is the ratio of the discrete phase to the continuous index of refraction.

For a more extensive deduction of the theory behind NIR measurements on asphaltene particles, the works of Mullins [30], Kallevik [31] and Joshi et al. [32] are recommended for further details.

Results and discussion

In this study NIR spectroscopy was applied as a tool to probe the effect of various chemicals on asphaltene aggregates as a function of time and additive concentration.

In setting up the matrix for the chemicals some fundamental interaction patterns were considered. The starting point is that the dominating attractive forces for asphaltene aggregation are hydrogen bonding, acid–base interactions and charge transfer between aromatics. The main strategy for the disintegration of asphaltene aggregates should hence be to break these bonds and stabilize the smaller asphaltenes aggregates. The supposed interactions for the individual chemicals are further specified as follows.

- *n*-Alkylbenzenesulfonic acid: Dodecylbenzenesulfonic acid is known to efficiently disperse asphaltenes and form stable suspensions [33]. The mechanism behind the efficiency is assumed to be a strong acid–base interaction between the sulfonic acid headgroup and basic material in the asphaltene molecule. The alkyl chain is long enough (n-C_{10-13}) to disperse the asphaltene molecules and to give steric stabilisation.
- Naphthenic acids: In crude oils the naphthenic acids are normally incorporated in the group of resin molecules. It is generally believed that these acids (a mixture of condensed ring structures with various numbers of rings and alkyl moieties, various positions of the COOH groups, various hydrophile–lipophile balance values, etc.) will possess various properties with regard to the asphaltenes. The strong interaction is between the acid groups and basic components in the asphaltene molecule. The dispersing power is determined by the molecular structure. Most probably various naphthenic acid structures will possess different dispersing powers. In this study we investigated the following naphthenic acids: 5-β-(H)-cholanoic acid (Chol), 1-napthalenepentanoic acid, decahydro (2C4), 1-naphthalenoic acid, decahydro-2-butyl (C42), crude naphthenic acid (CNA), Fluka naphthenic acid, and North Sea naphthenic acid. The structures and molecular weights are summarized in Table 1.
- Fatty alcohols: Fatty alcohols are normally efficient solvent molecules owing to their efficiency in breaking existing bonds and in forming new more favorable ones. Short-chain alcohols are believed to break down existing intermolecular hydrogen bonds between different asphaltene molecules and to replace them with alcohol–asphaltene hydrogen bonds. The alcohols used in this study were limited to 1-octanol, which is a normal paraffinic alcohol, 2-ethyl-1-hexanol, which is a branched paraffinic alcohol with the same number of carbon atoms, and benzyl alcohol, which is an aromatic derivative.
- Fatty amines: The functionality of these is very much the same as for the fatty alcohols, i.e. the capability of replacing the hydrogen bonds with the amine group and to disperse with the alkyl moiety.
- Inhibitor A. This is a commercial blend consisting of fatty amines and acids in polar solvents.

The results obtained can be summarised as follows. The relative OD at 1,600 nm versus time for toluene/*n*-heptane/asphaltene mixtures with different amounts of CNA is shown in Fig. 2. The influence of additive upon aggregate size is depicted as the decrease of scattering as a function of time. The relative OD vs. time for toluene/*n*-heptane/asphaltene mixtures with various naphthenic acids is plotted in Fig. 3. The commercial Fluka naphthenic acid and the naphthenic acid extracted from a North Sea crude seem to affect the state of the asphaltenes only to a minor extent. CNA is most efficient of these polydisperse naphthenic acids.

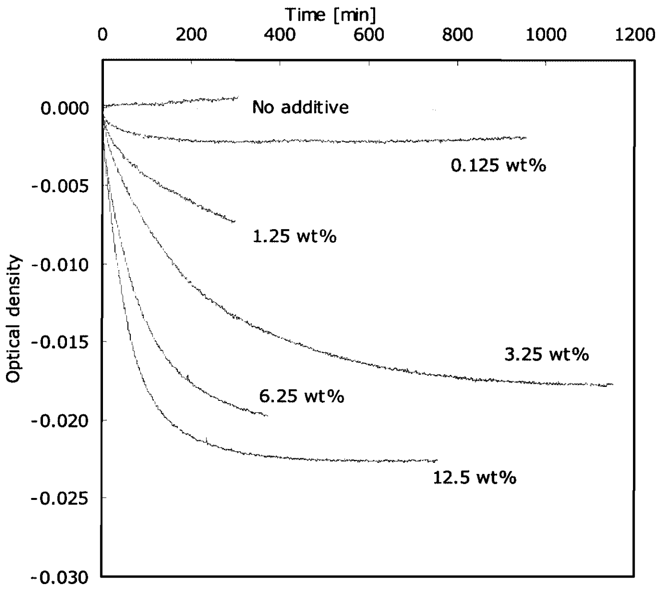


Fig. 2. NIR scattering measurements at 1,600 nm for 0.125 wt% asphaltenes in a 70/30 *n*-heptane/toluene mixture with crude naphthenic acid (*CNA*) added in various concentrations

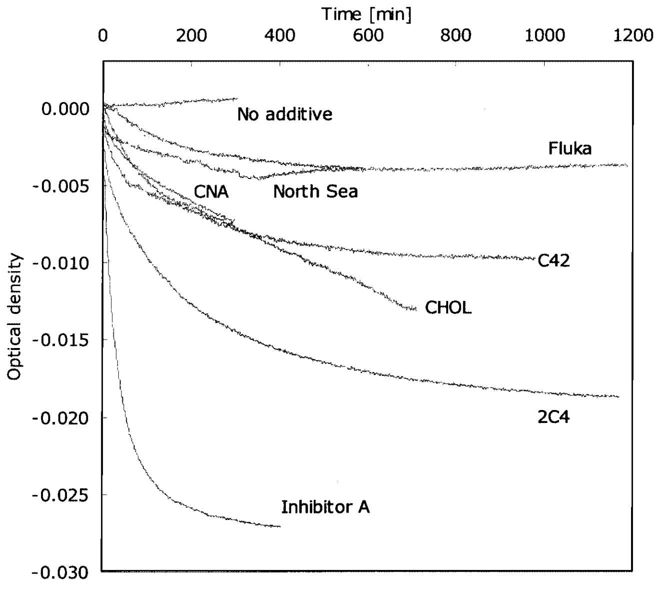


Fig. 3. NIR scattering measurements at 1,600 nm for 0.125 wt% asphaltenes in a 70/30 *n*-heptane/toluene mixture with 1.25 wt% of various naphthenic acids added: 5-β-(*H*)-cholanoic acid (*Chol*), 1-napthalenepentanoic acid, decahydro (*2C4*), 1-naphthalenoic acid, decahydro-2-butyl (*C42*), CNA, Fluka naphthenic acid (*Fluka*) and North Sea naphthenic acid (*North Sea*)

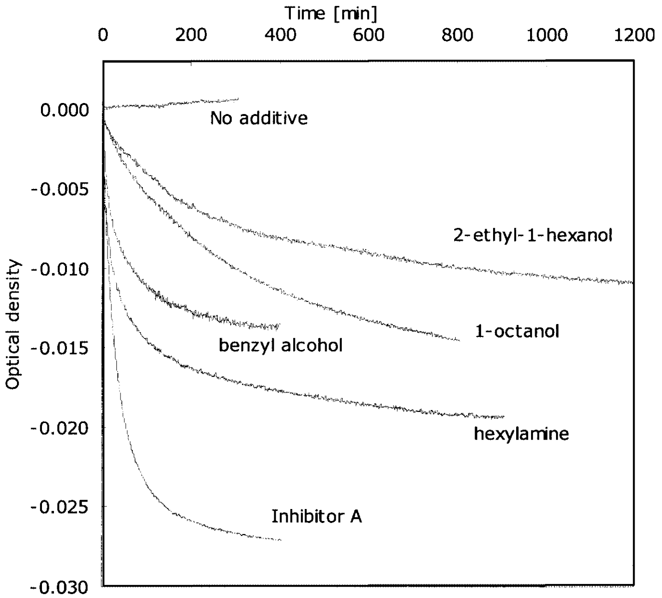


Fig. 4. NIR scattering measurements at 1,600 nm for 0.125 wt% asphaltenes in a 70/30 *n*-heptane/toluene mixture with 1.25 wt% various amphiphiles added

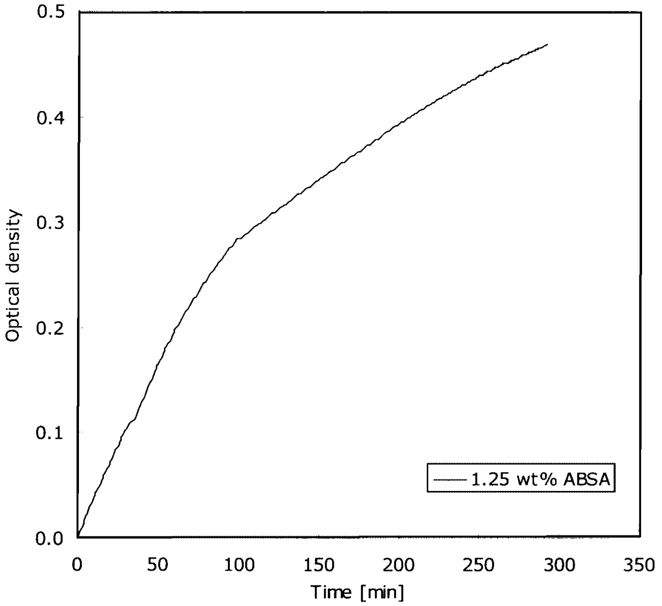


Fig. 5. NIR scattering measurements at 1,600 nm for 0.125 wt% asphaltenes in a 70/30 *n*-heptane/toluene mixture with 1.25 wt% *n*-alkylbenzenesulfonic acid (*ABSA*) added

A comparison between 2C4, C42 and Chol shows these species to be somewhat more efficient than the previous group. Especially the 2C4 molecule has a very efficient breakdown to start with and also attains a low final value. It is thrilling to see that the molecular structure affects the results to this extent.

The other amphiphiles, presented in Fig. 4, have a varying effect on the disintegration of the asphaltenes. The most efficient one is 1-hexylamine, which is very reminiscent of 2C4 with regard to short-term efficiency and the final state. The most efficient treatment is due to inhibitor A, the commercial mixture.

Alkylbenzenesulfonic acid is shown to associate with the asphaltenes and create aggregates of increased sizes (Fig. 5). This is in accordance with the results obtained by Chang and Fogler [25] in a UV/vis spectroscopic study. They suggested that asphaltenes and dodecylbenzenesulfonic acid could associate into large electronic conjugated complexes.

Conclusions

It was shown that NIR spectroscopy is a powerful method to follow the disintegration of asphaltene aggregates upon addition of chemicals. The method is based on the scattering from preferentially large aggregates. The NIR technique, which is very fast and accurate, is a good choice for the initial screening of large numbers of chemicals for asphaltene inhibition. The results show that additives which are efficient in replacing hydrogen bonds possess dispersive power and can serve as inhibitors. Commercial blends of active molecules gave the best results.

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