

Effect of Organic Additives on the Onset of Asphaltene Precipitation

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Onset of solid precipitation from oils was determined by identifying the minimum in near-infrared absorbance. Solvent-induced precipitation typically causes asphaltene precipitation, but is also known to cause high-molecular-weight waxes to come out of solution. The effects of the addition of solid saturated and unsaturated compounds on the onset of solvent-induced precipitation from a crude oil were examined. Crude oil from Rangely, an oil field in northwestern Colorado was used. The solvent-induced precipitation was brought about using pentane, hexane, and heptane. On the basis of limited solvent carbon number investigated (5–7), less solvent was required for precipitation onset as the carbon number of alkanes decreased. As the flow rate of the precipitant increased, the onset was delayed. Addition of solid *n*-alkanes, such as eicosane and tetracosane to the oil initially, accelerated the onset of precipitation. When solid polyaromatic compounds (naphthalene and phenanthrene) were dissolved in the oil, more solvent was required to initiate onset of precipitation. It was also shown that the crude oil was considerably undersaturated with respect to the asphaltenes and that initial dissolution of asphaltenes in the oil accelerated the precipitation. The data provided insight on solubility-related solids precipitation from oils.

Introduction

Crude oil asphaltenes are compounds classified by their solubilities in *n*-alkanes. The asphaltene precipitation problems are common both in the upstream (production and transportation) and the downstream (processing, refining) segments of the oil industry. Deposition problems are known to occur even when the amount of asphaltenes in the original mixture is relatively low.¹ Conversely, in some instances, oils with relatively higher amounts of asphaltenes show no signs of precipitation/deposition.¹ For instance, oil from the Boscan field in Venezuela showed no asphaltene precipitation problems even with an initial asphaltene content of 17.2 wt %, while, the Ula field in North Sea was plagued with solids precipitation problems with an oil containing a relatively small amount of asphaltenes (0.57 wt %).

The reason is the complexity of asphaltene compound class. This class of compounds is not easily characterized because of the high molecular weight and polarity of compounds. All aspects of asphaltenes have been extensively studied. Researchers have attributed the formation of solids to solubility-related phenomena as well as colloidal particle agglomeration. This paper examines changes in the solubility of asphaltenic compounds in oil as a result of induced compositional variations.

In terms of controlling or providing solutions to the precipitation problem, it is important to know when the precipitation is initiated and the quantity of asphaltenes which can be deposited during oil production, transportation, or processing. Accurate determination of the onset of precipitation is therefore important. Onset is defined as the minimum amount of precipitant necessary to induce the precipitation of solids, believed to be asphaltenes. A number of methods have been developed to measure the onset of precipitation or flocculation of asphaltenes. Precipitation onset data have been reported with conductivity,² refractive index,^{3,4} and viscosity⁵ measurements.

Spectroscopy has been a popular tool for the determination of the onset of precipitation. A UV spectrometer has often been used to determine the onset of solids precipitation. Andersen⁶ chose a wavelength of 740 nm for measuring the onset while Reichert and co-workers⁷ used 900 nm. They both used toluene as a dispersant. Direct measurements on precipitation onset with UV spectroscopy are difficult due to the dark nature of the original oil. Near-infrared (IR) spectroscopy is ideal for determining the onset directly. Effectiveness of the use

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of near-IR spectroscopy to accurately measure precipitation onset has been demonstrated.^{8–10} Typically, onset as a function of precipitant concentration is measured by titration of the oil with the appropriate solvent.

A number of investigators have studied precipitation of solids as a function of the carbon number of the alkane precipitant.^{11–14} It is well-known that as the alkane carbon number increases, the amount of precipitated material decreases. The molecular weight distribution of the precipitated material shifts to the left (indicating that relatively smaller compounds become part of the asphaltene class) as the *n*-alkane carbon number decreases.¹² It was also known that the oil phase becomes more stable with the addition of light aromatic compounds, such as toluene and xylene and it is comparatively more difficult to precipitate asphaltenes from these mixtures.

Clarke and Pruden¹⁵ reported the effect of additives on the onset of asphaltene precipitation from Canadian bitumens by the heat transfer technique. They used aromatics, heteroatomic compounds, hydrogen donor chemicals, and surfactants as additives. The results showed that the addition of aromatic compounds delayed the onset of precipitation from highly asphaltic oils (bitumens). Phenanthrene addition (20 wt %) to Cold Lake bitumen delayed the onset, and appeared to be more effective than the additions of toluene, xylene, or naphthalene. They hypothesized that phenanthrene's high aromaticity and molecular weight gave it resin-like features. The effects of the additions of heteroatomic compounds and hydrogen donor chemicals (tetralin, decalin) were relatively small. Addition of the surfactant, nonyl-phenol was most effective in delaying the onset while dodecylbenzene sulfonic acid was ineffective. Chang and Fogler¹⁶ suggested that the asphaltene stabilizing effects were dependent on the length of the alkyl tail and the polarity of the headgroup in the surfactants added. They found that the additives were most effective in delaying precipitation when the compound consisted of more than six alkyl chains with a sufficiently polar head, such as a hydroxyl or a sulfonate.

One of the objectives of this study was to examine the effects of solid organic additives on the onset of the precipitation of asphaltenic solids. The objective was also to explore solubility-related solids precipitation in a broad context. Apart from significant inorganic solids precipitation issues and problems related to gas hydrates, there are two organic solids precipitation phenomena of significance in the oil industry: (1) precipitation of waxes, which is primarily temperature induced,

and (2) precipitation of asphaltenes, which is driven by changes in oil composition. Under some circumstances, coprecipitation of these compounds may be important. Asphaltene precipitation is observed during primary depletion and in the course of miscible gas injection processes. The primary depletion is carried out at high pressures, and pressure is an important parameter. The quality of asphaltenes collected during miscible injection processes is different from the quality of laboratory asphaltenes (*n*-heptane insolubles), possibly due to the presence of higher-molecular-weight waxes. If asphaltene precipitation occurs at high temperatures (over 60 °C), coprecipitation of waxes is usually not an issue. In wax precipitation, there are questions about the quantity of asphaltenes that coprecipitate. In this study, that aspect was examined by measuring asphaltene precipitation onset on addition of *n*-alkane solid compounds. For comparison, addition of aromatic solid compounds was also investigated. The near-IR spectroscopy provided a quick, accurate, and direct measurement of the onset points. Oil with a relatively low amount of initial asphaltene content was employed. The first few experiments were performed with different precipitants and with liquid additives to streamline and validate the experimental procedures.

Experimental Section

A single crude oil was used in all the experiments. The crude oil was from the Rangely field in northwestern Colorado. The initial asphaltene content (heptane insolubles) of the oil was 1.7 wt %. Fractions of saturates, aromatics, and resins, as determined by column chromatography, were approximately 49%, 23%, and 3%, respectively (the remainder is accounted for by lights and the unrecovered portion of oil).

Phenanthrene, eicosane, and tetracosane were used without purification from Aldrich Chemicals. Naphthalene was used from Mallinckrodt, also without further purification. Toluene and *n*-heptane were HPLC grade and were more than 99% pure.

Near-IR spectra were collected over the 1200 to 2400 nm spectral region with a Quantum-1200 (from LT Industries, Inc.) spectrometer consisting of a fiber optic detector. The spectra were collected through a probe equipped with a sapphire lens. The path length was 6 mm. Scans were collected every 30 s.

A known amount (40 g) of the crude oil was charged to a flask and a normal paraffin solvent was added to the oil at a controlled, constant rate (titration). The oil-solvent mixture was mixed continuously with a magnetic stirring device. A schematic diagram of the experimental system is shown in Figure 1. To study the effect of the addition of different organic solids, the solid compounds were added until they dissolved completely in the crude oil (with an initial mixing period of several hours). In most experiments, about 2 g of solids dissolved in the oil completely. The flow of alkanes (precipitants) was controlled by a peristaltic pump. The near-IR spectra were obtained with the probe directly placed inside the mixture. After 300 mL titration with the precipitant, the mixture was filtered with a 2.7- μ m filter. The weighing was continued until the weight was constant.

Results and Discussion

A series of spectra at different precipitant concentrations for a typical experiment are shown in Figure 2. The precipitant used in this experiment was *n*-heptane. The *n*-heptane spectrum is also shown for comparison.

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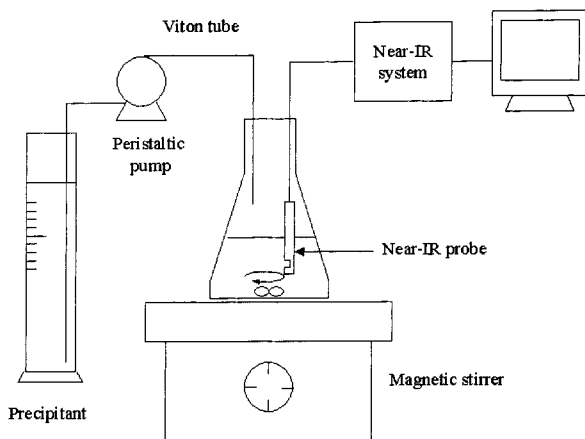


Figure 1. Schematic diagram of the experimental system used.

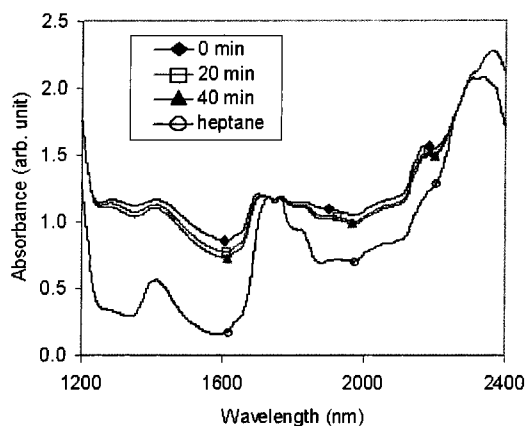


Figure 2. Near-IR spectra at various times as oil is titrated with *n*-heptane. Spectra over the 1200–2400 nm range are shown.

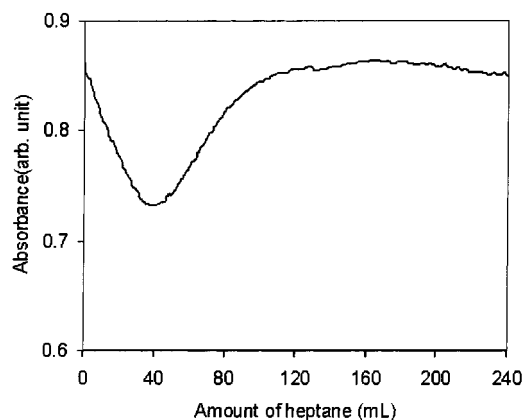


Figure 3. Near-IR absorbance at a wavelength of 1600 nm for oil titration with heptane (flow rate = 1 mL/min).

Most significant information is obtained by studying the absorbance values of the mixtures at around 1600 nm. Fuhr et al.⁹ used this wavelength for their diagnostics. A typical absorbance curve at a wavelength of 1600 nm is shown in Figure 3. This curve was obtained by the addition of *n*-heptane to 40 g of the crude oil at a flow rate of 1 mL/min. Absorbance data were collected every 30 s when *n*-heptane was added to the oil. The initial decrease in absorbance is due to dilution. The near-IR signal is affected by a number of factors and it does not decrease linearly as solvent is added. It has been argued

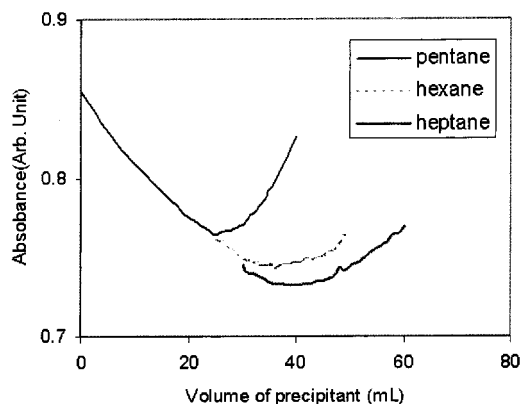


Figure 4. Near-IR absorbance curves at 1600 nm when three different precipitants are employed.

that⁸ the absorbing molecules in the oil undergo changes that affect the near-IR absorbance. During asphaltene precipitation, new (larger) particles that absorb/scatter light are formed and this event is adequate to turn the signal upward. The minimum in absorbance corresponds to the onset. As the particles grow and agglomerate, they tend to settle, leading to a slight decrease in absorbance as the titration continues. Thus, the mild maximum in the absorbance curve may correspond to the beginning of the settling process. In these types of measurements, the emphasis is only on identifying the starting point of precipitation. These methods (titration type) are a faster alternative to static measurements, and are more suitable for high-pressure/blind cell measurements. The error in these measurements was 0.0125 mL/g of oil.

The first few experiments were performed to study the effect of the *n*-alkane solvent carbon number on the onset and the effect of the addition of toluene. There has been some controversy in the literature regarding the effect of the solvent chain length on precipitation onset. Visually determined onset data by Hirschberg et al.¹³ showed that onset accelerated with increased solvent carbon number. The onset in these experiments was determined by observations through a microscope, which magnified the image 200-fold. Recent measurements by light absorbance/scattering showed that increasing the solvent carbon number delayed the onset.^{9,14,17} Precipitation onset points for the Rangely crude oil were measured using three solvents and the results are shown in Figure 4. In this figure, the absorbance at 1600 nm is plotted as the various solvents are added at 1 mL/min. In case of *n*-pentane, the onset is much faster (0.62 mL of precipitant per gram of oil) than with *n*-hexane (0.87 mL/g) or *n*-heptane (1 mL/g). Rassamdana et al.¹⁴ reported similar findings, even though their onset variations (with respect to alkane carbon number) were comparatively small. For the carbon number range studied, as the solvent carbon number increased, more of the solvent was necessary to initiate precipitation. The carbon number range studied was narrow and the trend may reverse for solvents with higher carbon number.¹⁴

The weight percents of asphaltenes precipitated with the three different alkanes after 5 h of titration at a

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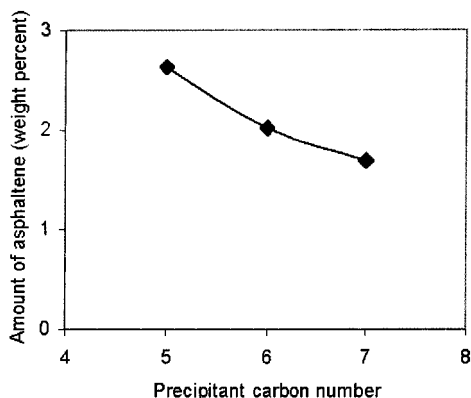


Figure 5. Asphaltene amounts versus *n*-alkane precipitant carbon number after 300 min of titration at 1 mL/min.

flow rate of 1 mL/min are shown in Figure 5. As is well-known, the amount of asphaltenes increased with decreasing *n*-alkane carbon number. The weight percents of asphaltenes precipitated were 2.63, 2.02, and 1.68 for *n*-pentane, *n*-hexane, and *n*-heptane, respectively. This means that compounds, which were not part of the solids with *n*-heptane, were precipitating when *n*-pentane is used. The flow rate of 1 mL/min was chosen after a number of experiments at different flow rates. It was observed that the onset was delayed at higher flow rates. The onset value stabilized at or below 1 mL/min and the differences were within the experimental error in onset determination (0.0125 mL/g of oil). This is to be expected since there are mixing and mass transfer limitations at higher flow rates. This is contrary to the observations of Andersen,⁶ who noted (using a different measurement system) that quicker onset is observed at higher flow rates. His measurements required the samples to be physically transported to the measurement device, while in these experiments, the near-IR absorbance was measured instantaneously.

To study the effect of the addition of toluene on precipitation, the Rangely crude oil was initially mixed with different amounts of toluene and the resulting mixtures were titrated using the procedure described. In this experiment, 40 g of the crude oil and 5–20 mL of toluene were separately mixed before titration. As the amount of toluene added increased, the precipitation onset was delayed more or less in a linear manner. The data are presented in Figure 6. Toluene is a polar compound that acts as a stabilizer in the oil. The toluene onset data (plotted in Figure 8 for comparison with other additives) showed that the oil was undersaturated with respect to asphaltenes.

Effect of addition of *n*-heptane-insoluble asphaltenes on asphaltene precipitation from the oil was examined. In these experiments, asphaltenes were first separated from the oil using a procedure described by Speight et al.¹⁸ In this method, the oil and the solvent (*n*-heptane) are mixed at a ratio of 1:40 and equilibrated for 16 h. The asphaltenes were filtered, washed with *n*-heptane, and were dried. The asphaltenes so obtained were stored in the laboratory at normal conditions. Dissolution of small amounts of heptane-insoluble asphaltenes in the oil accelerated the precipitation onset from the oil. The

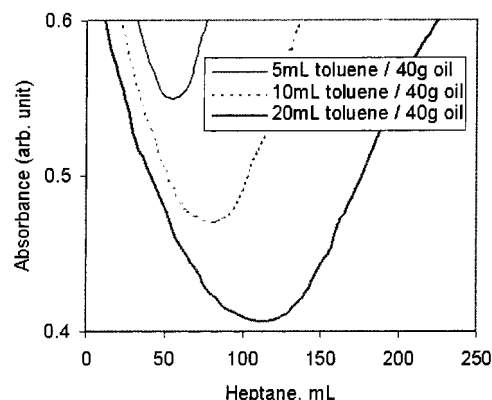


Figure 6. Near-IR spectra at 1600 nm for titrations of oil-toluene mixtures with heptane. As more toluene is added, precipitation is delayed.

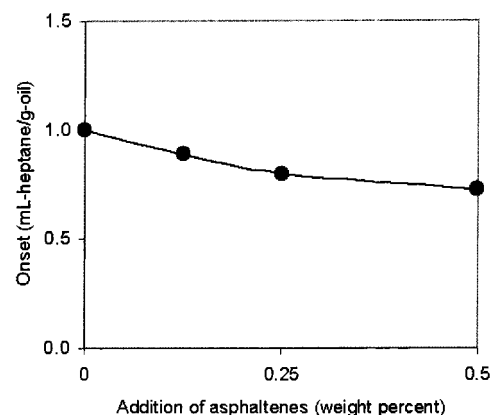


Figure 7. Plot indicating accelerated onset when additional *n*-heptane-insoluble asphaltenes are dissolved in oil.

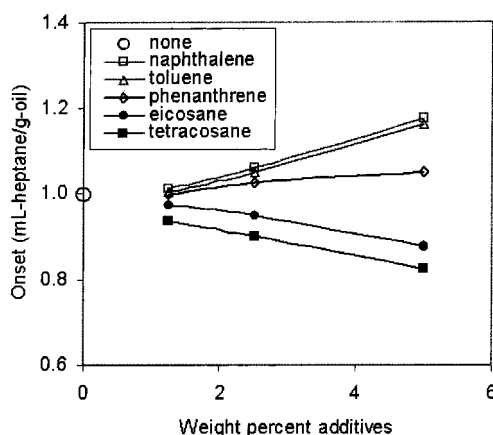


Figure 8. Effect of the initial dissolution of *n*-alkane-solids and polyaromatic compounds (weight percent) in the oil on the onset of asphaltene precipitation from the oil.

onset values for three solutions of asphaltenes and oil are provided in Figure 7. The onset declines from a value of 1.0 mL/g to about 0.75 mL/g by adding 0.5 wt % *n*-heptane insolubles to the oil.

Effect of the Addition of Hydrocarbon Solids. The effect of the addition of solid pure hydrocarbon compounds on the onset is shown in Figure 8. Onset data for toluene has also been shown on this plot for comparison. The addition of eicosane and tetracosane accelerated the onset of solid precipitation, while the addition of phenanthrene, naphthalene, and toluene led to delayed solid precipitation from the oil. Onset trend

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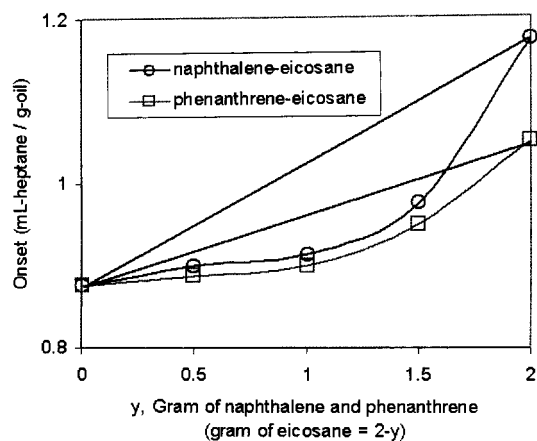


Figure 9. Asphaltene precipitation onset changes when combinations of *n*-alkane and polyaromatic solid compounds are used as additives.

with toluene addition can be viewed to evaluate if the oil is understaturated with respect to asphaltenes. The positive value of the *y*-intercept for the toluene line in Figure 8 can be interpreted to mean that that asphaltene phase in oil is stable and undersaturated.^{6,19} The effect of the addition of naphthalene and toluene on the onset appears more or less equivalent. Phenanthrene delays precipitation, but not to the same extent as toluene or naphthalene. Molecular weight of the additive also influences precipitation (apart from its solubility parameter). Rapid accelerations of precipitation observed with small additions of eicosane and tetra-eicosane indicate that seemingly minor changes to the solubility character of the solvent holding asphaltene in solution has a profound impact on asphaltene precipitation. The finding that naphthalene was more effective than phenanthrene in keeping asphaltene in solution was contrary to results reported by Clarke and Pruden¹⁵ for precipitation from Cold Lake bitumen. It appears that the effectiveness of an additive in delaying precipitation depends on the initial composition of the oil. In this study, the measurements were direct and light oil with relatively low amount of asphaltene was used. Addition of asphaltene to the original oil, however, accelerated the precipitation (Figure 7), as shown earlier.

Experiments were also performed with mixtures of polar and nonpolar solids. These experiments were performed with the total weight of solid additive fixed at 2 g. Each solid mixture was initially mixed with 40 g of oil. The onset data for these experiments is plotted in Figure 9. The *x*-axis on this figure shows the grams of naphthalene or phenanthrene added (*y* grams). Since the total weight of solid additive was constant at 2 g, the weight of eicosane added was equal to 2 - *y* grams. It should be noted that when no solids are added, the precipitation with heptane occurs at 1 mL/g. If the effect of adding mixtures of polyaromatic compounds (naphthalene or phenanthrene) and eicosane on asphaltene precipitation onset was linear, then the onset data for mixtures would lie on straight lines connecting the onset point for the addition of pure eicosane (*y* = 0) and onset points for the additions of pure naphthalene or phenanthrene (*y* = 2). These lines are shown in Figure 9. Since

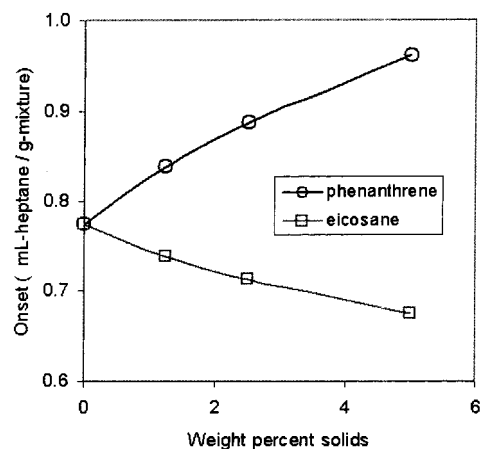


Figure 10. Asphaltene precipitation onset from asphaltene-toluene mixtures with the addition of *n*-alkane solid or polyaromatic compounds.

most of the onset points for the mixtures lie below these straight-lines, it is clear that eicosane has a more dominant effect on onset than either naphthalene or phenanthrene.

The experiments were repeated using asphaltene dissolved in toluene. In these experiments, asphaltene solids from the Rangely field were dissolved in toluene and a 2 wt % mixture was prepared. The asphaltene solids were formed in the course of a carbon dioxide flood in the field. The effects of the addition of *n*-alkane and polyaromatic solids were examined with this mixture. Eicosane or phenanthrene (0.5 g to 2 g) was added to the mixture (40 g) and the precipitation onset was measured using *n*-heptane as the precipitant. The data are presented in Figure 10. The trend in precipitation initiation with additions *n*-alkane and polyaromatic solids is observed to be similar to the oil data. These experiments show that it is possible to dissolve asphaltene in appropriate solvents and reprecipitate them using *n*-alkane additives. The type of compositional changes that cause either delayed or accelerated precipitation are observed in oils and in asphaltene-solvent mixtures.

This study is an examination of the onset of asphaltene precipitation and how it is affected by solid organic additives to the whole oil. As lighter *n*-alkanes are used, the amounts of solids precipitating increase indicating that some compounds which remained in solution with higher *n*-alkanes, become part of the class. It is logical also that precipitation occurs sooner with lighter alkanes than with the heavier ones. Whatever changes the quality of the solution changes the solution dynamics of the compounds in solution. Addition of small quantities of straight-chain, *n*-alkane solid compounds decreases the relative solubility of the asphaltene compounds and expedites their precipitation. Addition of polyaromatic compounds increases the overall solubility of the solution and delays precipitation of asphaltene material.

The data reported in this paper underscore the nature of asphaltene as a solubility class. Wiehe^{20,21} in his

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Table 1. Solubility Parameters and Melting Temperature of Solids in This Study^a

	molecular weight	solubility parameter (cal/cm ³) ^{0.5}	melting point (°C)
toluene	92.14	8.93	-95
naphthalene	128.17	9.9	80.5
phenanthrene	178.23	9.92	100
eicosane	282.55	8.06	36.8
tetracosane ^b	338.66	7.42	54

^a References 22–24. ^b At 374 K from ref 25.

pioneering work has developed a great deal of understanding regarding the solubility of organic polymers and petroleum fractions in a variety of solvents. His two-dimensional solubility parameter theory explains how aromaticity and molecular weights of fractions determine their solubility. Basic compound properties of the additives used in this study (including the solubility parameters) are listed in Table 1. The solubility parameters of naphthalene and phenanthrene are about 9.9 (cal/cm³)^{0.5}, which are in the same range as the solubilities of the asphaltenic compounds. The solubility parameters of eicosane and tetracosane are 8.06 (cal/cm³)^{0.5} and 7.42 (cal/cm³)^{0.5}, respectively. On the basis of several studies in the literature,^{13,17} asphaltene solubility parameter is approximately between 9.0 (cal/cm³)^{0.5} and 10 (cal/cm³)^{0.5}. The higher the contrast between the solubility parameters of the asphaltenic compounds and the additives, the easier and quicker it is to bring them out of solution. When adding multiple additives, the low solubility parameter compounds govern the behavior of the solution and it is not possible to offset the effect by adding compounds with higher solubility. However, solubility parameter is not the sole determinant of the effect of the additive. The molecular weight and other properties of the additives become important. The delay in precipitation becomes more gradual as the solid additive is changed from naphthalene to phenanthrene. Addition of asphaltenes to the oil expedited the precipitation of the dissolved asphaltenic compounds from the oil.

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The data can also be examined with respect to the coprecipitation implications. Since adding solid *n*-alkanes brings about a quicker onset of asphaltene precipitation, it can be assumed that taking them out of the oil, selectively, helps keep asphaltenes in solution. It is quite clear that the precipitation of *n*-alkanes from the oil on cooling (wax precipitation) is governed by the solubilities of these alkanes in oil. As the alkanes come out of solution, the polar components that have higher solubility in the oil have even greater solubility in the remaining oil (liquid) mixture, making their precipitation unlikely. It should be noted that from an overall compound classification viewpoint, the oil that was examined contained close to 50% saturated compounds.

Conclusions

The onset of asphaltene precipitation from a light crude oil was determined using near-IR spectroscopy. In the carbon number range studied (5 to 7), more solvent was necessary to initiate precipitation onset as the carbon number of the solvent increased, resulting ultimately in higher amounts of asphaltenes precipitated. Addition of toluene delayed precipitation and also showed that the oil was undersaturated with respect to the asphaltenes. When aromatic solids (phenanthrene and naphthalene) were initially mixed with the oil, the onset of solid deposition was delayed. In the case of the addition of solid *n*-alkane compounds (eicosane and tetracosane), the onset of solid precipitation was accelerated. Addition of separated asphaltenes to the oil, however, accelerated the precipitation onset. When mixtures of polar and nonpolar solids were added, the precipitation was governed by the nonpolar compound additive. These observations were true for the reprecipitation of dissolved/dispersed asphaltenes as well. The measurements show that the complex phenomenon of dissolved asphaltene precipitation is controlled to a significant extent by simple solubility rules.

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