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Asphaltene characterization of paraffinic crude oils

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HIGHLIGHTS

- Analyses of solid phases from paraffinic oils revealed the presence of asphaltenes.
- Asphaltenes with large solubility parameters precipitate together with waxes.
- Asphaltenes in deposits show larger solubility parameters than ones in the oil.
- Composition of precipitated asphaltenes changes as a function of time.

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ABSTRACT

Precipitation and deposition of asphaltene and waxes pose a serious challenge to the petroleum industry since costly remedial actions to maintain operations are required. Even though asphaltenes and waxes are radically different in chemical nature, they both have low solubility in crude oils, and they frequently appear together in recovered deposits from wells and pipelines. In this work, we evaluate the solubility characteristics of the asphaltenes that are naturally associated themselves with the wax crystals present in several paraffinic crude oils. Filtration was used to separate precipitated waxes from crude oils at room temperature, and the solubility distributions of asphaltenes associated with the precipitated waxes are compared with the distributions of the total asphaltenes present in the original crude oils. It was found that the filtered cakes were enriched in the least soluble asphaltenes as indicated by their larger average solubility parameters in comparison with the crude oil (21.3–21.6 $MPa^{0.5}$ vs. 18.5–18.6 $MPa^{0.5}$). These are the type of asphaltenes likely to be present in deposits together with waxes. Additionally, after filtration, the filtered crude oil was spiked with pentane asphaltenes and after one week, the precipitated solids were separated again and analyzed. The results indicated that the precipitated solids were enriched in higher solubility parameter asphaltenes in comparison to the pentane asphaltenes originally added. This separation is likely the product of the low solvent power of the maltenes of these crude oils. Comparison of the precipitated asphaltenes from original and spiked crude oils revealed that those that precipitated in association to wax crystals had larger solubility (21.3–21.8 $MPa^{0.5}$ vs. 20.0–20.1 $MPa^{0.5}$) parameters than those recovered after spiking.

1. Introduction

The supply of paraffinic crude oils to refineries has grown considerably in the last few years as a consequence of the increasing production of tight oils [1]. These paraffinic crude oils can bring significant challenges to downstream operations. Fouling studies have shown that paraffinic crudes, even containing low amounts of asphaltenes, had relatively high fouling rates [2,3]. Additionally, light paraffinic oils are normally blended with heavier crude oils and therefore, can potentially induce asphaltene precipitation. Also, wax presence enhances the formation of stable emulsions during desalting operations [4] and decreases the desalting efficiency [5]. Further fouling can also be expected in other refinery units as a consequence of wax–asphaltene interactions.

Analyses of sediments recovered from storage tanks indicated that waxes and asphaltenes often precipitate together forming a composite material [6]. A similar situation was reported during the calorimetric analysis of waxy and asphaltenic deposits from oil wells [7] where paraffins with more than 40 carbon atoms dominate the precipitate composition.

The interaction of waxes and asphaltenes in the crude oil has been the subject of numerous studies in the last two decades. These studies have provided significant insight on how asphaltenes affect the wax appearance temperature [8–11], rheological

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properties [10,11], and wax crystallinity [12]. In addition, waxes can modify asphaltene behavior [13–15]. For instance, they can accelerate dissolution of asphaltenes [13] and modify their stability [15].

Asphaltenes and paraffins generate solid complex mixtures whose formation seems to depend mainly on asphaltene properties and less on wax composition [13]. Dissolution studies of the composites have shown that the presence of waxes can accelerate the dissolution rate of the asphaltenes. This phenomenon can be explained by the interaction between peripheral alkyl chains in asphaltene aggregates and waxes. The interaction increases the volume of the alkyl layers surrounding asphaltene polyaromatic cores, and the swelling improves the dissolution of the solids [16,17].

Calorimetric studies [14,15] showed that the mixing of n-alkanes with asphaltenes is an exothermic phenomenon. Again, this is explained by the trapping of n-alkanes in the aliphatic shell formed by peripheral alkyl chains of asphaltenes. The trapping of alkanes in the exterior shell of the asphaltenes facilitates the nucleation and deposition of waxes while it can alter the stability of asphaltenes and induce flocculation. In fact, it is well known that alkanes precipitate asphaltenes and the amount, and characteristics of the precipitated asphaltenes depend on the solvent power of the alkane as well as other variables that include, but are not limited to alkane/sample ratio, contact time, and temperature [18–20].

As shown before, previous studies have led to the conclusion that asphaltenes and waxes interact synergistically. However, many of these investigations comprised the use of model systems where isolated asphaltenes and alkanes/or waxes are blended.

In contrast to these studies where natural conditions are manipulated, the main goal of the present work is to find out the asphaltenes characteristics that naturally associated themselves with the wax crystals present in the crude oil. To this end, filtration was used to separate precipitated waxes from crude oils at room temperature and the solubility distributions of asphaltenes associated with the precipitated waxes are compared with the distributions of the total asphaltenes present in the original crude oils. Additionally, we added asphaltenes to the crude oil after the precipitated solids (original waxes and asphaltenes) were separated to determine the effect that maltenes and time have on the composition of asphaltene particles.

2. Experimental section

2.1. Materials

Crude oils exhibiting wax crystals at room temperature were obtained from refinery tanks. These crude oils were associated to increase fouling in pre-train heat exchangers of the refinery. Pentane asphaltenes were obtained from a heavy crude oil (7.5°API) using the standard test ASTM D4055 [21]. Methylene chloride, toluene, chloroform, methanol, and n-heptane HPLC grade solvents were purchased from Fisher Scientific and used without further purification.

2.2. Separation scheme

Original crude oil samples were filtered using a centrifuge device with an average pore size of 0.22 μm so that particles could be recovered and analyzed. Tubes were centrifuged during 1 h at 1500 rpm. The precipitated material and filtered crude oils were recovered. Pentane asphaltenes were added to the filtered crude oil, sonicated for several hours and kept into storage for 1 week in an inert atmosphere. Then, the spiked crude oils were filtered using the same procedure employed for the original crude oil. A second set of precipitated materials and filtered spiked crude oil was recovered. Filter cakes (precipitated materials) and filtrates were analyzed. Fig. 1 shows the separation scheme.

2.3. Characterization methods

Optical microscope observations were made using a Zeiss Axioplan optical microscope with polarized light. Magnification was 200×.

Asphaltene concentrations and asphaltene solubility profiles were determined using on-column filtration techniques [22,23]. In these techniques, a solution of the sample is injected into a column packed with an inert material using n-heptane as the mobile phase. This solvent induces the precipitation of asphaltenes and, as a consequence, their retention in the column. To determine the asphaltene content the mobile phase is switched to a blend dichloromethane/methanol 90/10 v/v that redissolves the asphaltenes completely. To determine the asphaltene solubility profile, the mobile phase is changed gradually from pure n-heptane to 90/10 methylene chloride/methanol and then to 100% methanol. This procedure gradually re-dissolves the asphaltenes from the easy to dissolve (low solubility parameter) to the hard to dissolve (high solubility parameter). In both techniques, asphaltenes are quantified using an Evaporative Light Scattering Detector Alltech ELSD 2000. Rather recently, the method has been calibrated to produce a distribution of asphaltenes in terms of their solubility parameters. A description of the calibration is published elsewhere [24].

Carbon, hydrogen, and nitrogen (CHN) analysis was carried out with a Carlo Erba model 1108 analyzer. Metal and sulfur contents were determined using a Thermo Intrepid ICP.

High-temperature gas chromatography (HTGC) was performed using a J&W Scientific DB-1HT 30 m × 0.320 mm ID × 10 μm film thickness column. A Hewlett Packard/Agilent 6890 with a 7673 autosampler and Flame Ionization Detector (FID) system was used. Samples were dissolved in HPLC grade CS_2 and injected on-column (1.0 μl). Data were collected and analyzed using an Agilent EZChrom Chromatographic Data System.

3. Results and discussion

3.1. Crude oil characterization

Table 1 shows the main characteristics of the crude oils used in the study. All these crude oils exhibit wax crystals at room temperature and contain small amounts of asphaltenes. Fig. 2 shows examples of microscopic observations for two of the crude oils under polarized and normal light. In these microphotographs, the presence of wax crystals is indicated by bright spots under polarized light. Dark particles that appeared under regular light are identified as asphaltene particles.

3.2. Precipitated phase of original crude oils

Table 2 shows the characterization of the filtered cakes obtained by filtration of the original crude oils. In this table, large H/C ratios indicate the aliphatic character of the filtered cake that is expected, as the majority of particles present in the crude oils were identified as wax crystals. Measurements of the asphaltene content on the filtered cakes revealed that they contain small asphaltene amounts ranging from around 4 to 20 wt%. In all the cases, there is a clear enrichment in the amount of the asphaltenes in the filtered cake with respect to the original crude oil. However, even though filtration–centrifugation provides a direct