



Evaluation of asphaltenes stability by titration with propane under different pressures: a study using model systems

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Abstract

Asphaltenes are characterized as the highest molar mass and polarity fraction of crude oil, and their chemical structures are not well defined. The flocculation and deposition of asphaltenes can cause a lot of damage to the oil industry. Therefore, understanding the phase behavior of asphaltenes under conditions closer to those found in reservoirs is desired. The LMCP/UFRJ started to operate a unit to separate polar fractions of oil under high pressure and temperature. The asphaltenes precipitation onset was monitored by near-infrared spectroscopy. Due to the complexity of crude oil composition, this work used model systems prepared with asphaltenes extracted with n-pentane (C5) and n-heptane (C7). The experiments were carried out at ambient pressure titrated with n-heptane and at 100 and 300 bar, titrated with propane. As expected, asphaltenes C7I are more unstable, presenting lower precipitation onset than asphaltenes C5I at ambient conditions, and this result was confirmed at higher pressures. However, at higher pressures, for both model systems (with C5I and C7I), a greater volume of titration solvent is required to achieve the asphaltenes precipitation onset when compared with the results at ambient conditions. This indicates that an increase in pressure changed the phase behavior, increasing the stability of the system, when using propane as titration solvent.

Keywords

asphaltenes; phase behavior; propane titration

Introduction

Crude oil components can be divided into various compounds and subdivisions based on composition. Different types of solids can also exist in crude oil; however, the most prominent is solid asphaltene [1]. Asphaltenes are considered one of the most complex components of the crude oil because of many different structures, which makes very difficult to generalize to a specific group.

Therefore, asphaltenes are generally classified by their solubility class rather than a specific structure: they are insoluble in low molar mass n-alkanes and soluble in aromatic compounds as benzene and toluene [1,2]. The worldwide cost associated with deposition of asphaltenes during production and processing operations is on the order of billions of dollars per year. Asphaltenes deposition can reduce well productivity, restrict or plug production lines, and clog production oil treatment facilities. Asphaltenes precipitation can occur by changes, even if subtle, in pressure, temperature, oil composition, shear rates etc. [3].

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Variations in the composition of the oil can affect this balance and result in the precipitation of asphaltenes. Gas injection, one of the improved oil recovery techniques, is closely involved with the precipitation of asphaltenes in the reservoir. Nitrogen, natural gas and carbon dioxide are typical gases used in enhanced oil recovery techniques [4]. Regarding oil properties, these will change depending on the production mechanism, fluids injected into the reservoir and pressure changes as the hydrocarbon is produced. Various solvents can be injected into the reservoir, including steam, surfactant, CO₂, nitrogen, methane. As the solvent begins to interact with the oil, asphaltenes may no longer be stable in the crude oil due to a change in equilibrium conditions [1,5]. The problems due to the presence of asphaltenes in the oil come from its destabilization affecting different aspects in the flow assurance. The mitigation of these problems is one of the objectives involved in oil production. One of the first steps in preventing asphaltene deposition is to obtain accurate information about the structure of asphaltenes and their properties, such as stability. One of the methods to evaluate the asphaltenes stability measures the precipitation onset, which can be defined as the minimum amount of

precipitant that is required to induce the beginning of the asphaltenes precipitation [6].

Near infrared (NIR) spectroscopy is an appropriate technique to measure the asphaltenes precipitation onset during titration of a flocculant solvent. The test is relatively simple, time-efficient, highly accurate, informative and non-invasive. However, it is important to note that the method to determine precipitation onset, in general, is carried out in the laboratory, at ambient conditions, with controlled parameters, which makes the analysis reproducible. Under reservoir conditions, asphaltene precipitation occurs under conditions of high temperatures and pressures, being these characteristics particular to each field [7]. In this sense, this work aimed to establish an operational procedure for the high pressure and high temperature unit located at LMCP/IMA/UFRJ and to study the phase behavior of polar fractions in model systems under pressure conditions close to those found in reservoirs, evaluating the asphaltenes precipitation onset using propane as flocculating agent of asphaltenes in model systems using toluene as solvent.

Methodology

The oil sample for extracting asphaltenes was provided by Cenpes/Petrobras and identified as crude oil P01. Some physicochemical properties of crude oil P01 were provided by the supplier: °API = 21.1; pour point = -45°C; SARA = saturated 45.5%, aromatics 32.8%, resins 19.2% and asphaltenes 2.4%.

Experimental Procedure

Obtaining the asphaltene fractions

The asphaltenes were separated from the P01 oil sample based on a modification of the IP 143 standard. The main modification of the method was the adaptation for extraction of asphaltenes by n-pentane, since the IP 143 standard indicated n-heptane. About 30 g of P01 were added to 1L of n-pentane or n-heptane (precipitating agents), and kept under moderate agitation for 48 h. The precipitate was filtered under vacuum at room temperature using appropriate filter paper. The filtration process was repeated to minimize losses of the precipitated asphaltenes. In this step, the precipitate (unpurified asphaltenes) was obtained. The filter paper containing the precipitated sample was placed in the extraction cartridge. The insoluble fraction was washed successively in a Soxhlet extractor with 500 mL of the n-alkane initially used (n-C5 or n-C7) to remove resins coprecipitated with the asphaltenes. The purified solid residue was solubilized in 500 ml of toluene and separated from impurities that might have been contained in the residue. The solution of asphaltenes in toluene was placed in a glass container wrapped in aluminum foil to prevent its oxidation by the action of light and left in a fume hood under exhaustion at room temperature until

complete evaporation of the toluene. When dry, the asphaltenes fraction (C5I or C7I) was removed from the glass container. Then the sample was placed into a glass bottle and again wrapped in aluminum foil to prevent oxidation.

Fourier transform infrared spectroscopy (FT-IR)

FTIR spectra of the asphaltenes fractions C5I and C7I were obtained in a Thermo Fisher Scientific model Nicolett IS 50. The spectra were obtained at room temperature, in attenuated total reflection (ATR) mode by scanning from 4000 to 400 cm^{-1} with resolution of 4 cm^{-1} .

Elemental analysis (CHNSO)

Elemental analysis was used to determine the composition of fractions C5I-P01 and C7I-P01 in terms of weight percentage of carbon, hydrogen, nitrogen, sulfur and oxygen. The first four elements were quantified on a PerkinElmer CHNS/O 2400 Analyzer based on ASTM 5291 methodology. Oxygen was indirectly determined by difference and therefore is subject to a higher error than the other elements. This analysis allows the determination of the degree of unsaturation of the sample by calculating the C/H or H/C ratio [8].

Asphaltene precipitation onset

Model systems containing 1.00 wt/v% of asphaltenes C5I-P01 or C7I-P01 in toluene were used for these tests. The phase behavior of the asphaltic fractions by asphaltene precipitation onset was evaluated under different pressure conditions using a flocculation titrator with a pressurized cell in the "Polar Fraction Separation" Top Industrie equipment. For the experiments at 100 and 300 bar, the propane flow rate was equal to 2 mL/min. The changes in the systems were monitored by near-infrared (NIR) spectroscopy. Studies were also carried out at ambient pressure and temperature by titrating n-heptane to the model systems (at a flow rate of 1 mL/min) and monitoring precipitation using NIR. The tests at ambient conditions were carried out starting from approximately 7 g of the model system. Both analysis lasted from 40 to 60 min

Results and Discussion

Fourier transform infrared spectroscopy (FT-IR)

The absorption spectrum obtained for asphaltenes C7I-P01 showed essentially the same peaks of asphaltenes C5I-P01 excepting by relative intensities. The asphaltenes C7I-P01 spectrum showed more accentuated peaks in the bands corresponding to the markings 1600, 860 and 750 cm^{-1} , related to the aromatic compounds. Furthermore, the relative intensities of the 1600/2920 and 2850 cm^{-1} peaks were higher for the C7I-P01 asphaltene spectrum than for the C5I-P01 spectrum. This indicates a greater amount

of aromatic groups in asphaltenes extracted with n-heptane in relation to the fraction extracted using n-pentane as a precipitating agent, evidencing, as expected, that the asphaltene C7I is more polar than the C5I sample. Thus, given the extraction method, the more polar compounds are more concentrated in the asphaltenes C7I fraction while the less polar compounds are more concentrated in the C5I fraction [9].

Elemental analysis (CHNSO)

Elemental analysis was performed for asphaltenes fractions obtained from crude oil P01. The results are presented in Tab. 1.

Table 1. Carbon, hydrogen, nitrogen content and H/C and N/C ratio in asphaltenes samples C5I-P01 and C7I-P01.

Elements (%)	Asphaltenes	
	C5I-P01	C7I-P01
C	88.07	87.77
H	9.69	9.14
N	1.97	2.09
S - O	0.27	1.00
H/C	0.110	0.104
N/C	0.022	0.024

The higher H/C ratio, the greater the saturation of the sample (more C-H single bonds than C-C double or triple bonds). These results are in agreement with the fact that the asphaltene molecules contain polyaromatic rings, where double bonds between carbons predominate. The comparison of the results obtained for the fractions C5I-P01 and C7I-P01 shows that the carbon and hydrogen contents tend to decrease slightly with increasing polarity, while the nitrogen content tends to increase. The heteroatoms (nitrogen, sulfur and oxygen) may be responsible for the increase in polarity, to the detriment of the influence only of the aromatic compounds. Furthermore, the H/C ratio corroborates the FTIR analysis. Differences in H/C ratios may be due to higher levels of cyclic compounds in the more polar C7I fraction. The H/C ratios suggest that C7I-P01 asphaltene contains more fused polynuclear aromatic rings, while C5I-P01 asphaltene has less condensed aromatic rings with longer paraffinic side chains in their molecular structure.

Determination of asphaltene precipitation onset under ambient condition

The phase behavior of the solution titrated by n-heptane as a function of time was observed and graphs of absorbance versus volume of n-heptane by mass of the model solution were built as shown in Fig. (1). The minimum absorbance point on the graph indicates the asphaltene precipitation onset.

Table 2 summarizes the precipitation onset results for the model systems containing asphaltene extracted from crude oil P01 (C5I-P01 and C7I-

P01). The result is expressed as the average of two measures.

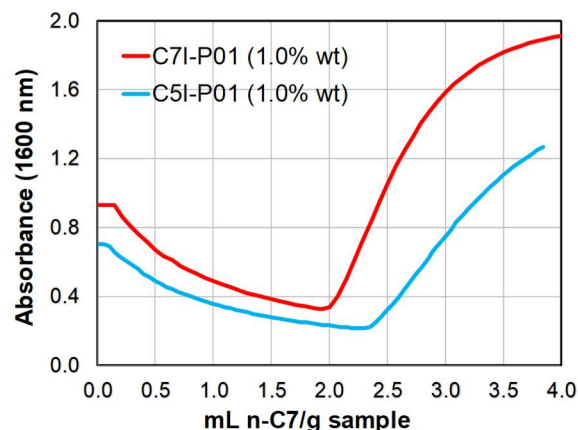


Figure 1. Determination of asphaltene precipitation onset from the model system C5I-P01 and C7I-P01 titrated with n-heptane.

Table 2. Onset values obtained and experimental error.

Sample	Precipitation onset (mL n-C7/ g sample)
C5I-P01	2.25 ± 0.01
C7I-P01	1.93 ± 0.01

The difference between the values found is according to the specificity of the n-alkane used in the extraction and the methodology used in the separation of the asphaltene fraction. The fraction insoluble in n-heptane (C7I) tends to be more polar than the insoluble in n-pentane (C5I). This is a characteristic caused by extraction with n-alkanes. Commonly, n-alkanes with lower carbon numbers provide higher yields in the extraction of asphaltene, encompassing a greater variety of molecules referring to molecular mass, but it is observed that this greater dispersion of molecular mass reduces the polarity of the fraction. Thus, when the flocculant agent is added to the solution, the more polar fraction, and consequently the most unstable, first separates from the phase, which characterizes a smaller volume of flocculant necessary for this phenomenon to occur. Therefore, the lowest value of onset found for the model system C7I-P01 compared to the system C5I-P01 is in agreement with the literature [10-13].

Determination of asphaltene precipitation onset in model systems titrated propane under high pressure

Figure 2 shows the absorbance versus volume of titrant per mass of model system curves obtained for model systems C5I-P01 and C7I-P01 titrated by propane at 100 and 300 bar. Similar to that observed for the test under ambient conditions (Figure 1), the asphaltene precipitation onset is gotten at the minimum absorbance.

Table 3 summarizes the asphaltene precipitation onset obtained for the model systems prepared

with C5P-01 or C7I-P01 by propane titration at 100 and 300 bar. The experimental error is given as the standard deviation value between two measures.

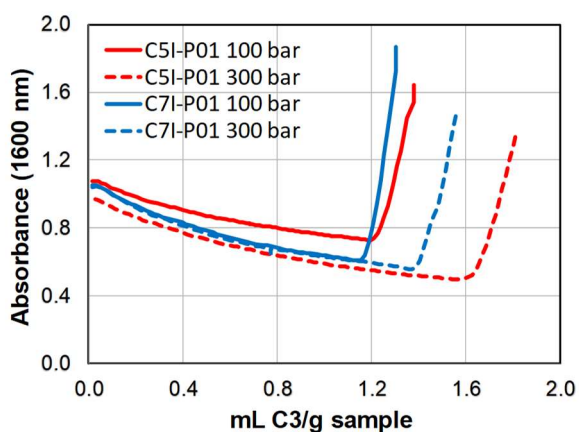


Figure 2. Determination of asphaltene precipitation onset of model systems C5I-P01 and C7I-P01 titrated with propane at 100 and 300 bar.

Table 3. Precipitation onset values of C5I-P01 and C7I-P01 titrated with propane at 100 and 300 bar pressure.

Sample	Pressure (bar)	Precipitation onset (mL n-C7/ g sample)
C5I-P01	100	1.22 ± 0.03
	300	1.54 ± 0.04
C7I-P01	100	1.13 ± 0.04
	300	1.41 ± 0.05

As discussed in the characterization of the C5I and C7I fractions obtained for this work, the asphaltene extracted from the oil with n-heptane are more unstable, more polar and show greater heterogeneity, when compared to the fraction extracted with n-pentane. This explains the values found in Table 3. The model system C7I-P01 showed a lower value of precipitation onset when compared to the model systems C5I-P01 at the same pressure. As it is more unstable, the asphaltene fraction C7I changes phase with the addition of a smaller volume of flocculating agent than the fraction C5I. When evaluating the same fraction, but at different pressures, the phase behavior was verified as follows: an increase in pressure provoked a higher onset value. For an increase of 200 bar of propane pressure on the system, a larger volume of flocculating agent was necessary to phase separate the asphaltene. When asphaltene, either the C5I or C7I fraction, are titrated at higher pressures (300 bar) with propane the stabilization of these molecules in the solvent medium increases, characterized by a higher precipitation onset value.

Conclusions

The equipment built and supplied by Top Industrie emerges as a new and promising alternative to

determine the asphaltene precipitation onset at high pressures and temperatures. By titrating model systems (asphaltene C5I or C7I in toluene) with propane at 100 and 300 bar, it was verified an increase in stability as increasing pressure. The tendency to reduce the precipitation onset value for the more polar asphaltic fraction C7I was observed both under ambient conditions and under high pressures.

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Responsibility Notice

The authors are the only responsible for the paper content.

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