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Solubility of Asphaltenes Fractions in Maltenes: a model system study

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Abstract
Crude oil can be seen as asphaltenes dispersed in a mixture of solvents called maltenes. The solubility of asphaltenes in maltenes will depend on the conditions of the medium, given that asphaltenes are soluble in aromatic and insoluble in aliphatic hydrocarbons, while maltenes are soluble in aliphatic ones. Asphaltenes precipitation is a problem in the oil and gas industry, as it tends to form deposits in pipelines, tanks, reservoirs and production equipment. Information on the solubility of asphaltenes in maltenes is valuable, but there is no detailed assessment of the solubility as a function of the asphaltenes fractions in the literature. In this work, fractions C3I, C6I and C7I were extracted from a crude oil sample and their solubility in maltenes was evaluated at room temperature and 60 °C. The C3I fraction was the only one completely soluble in the maltenes and the fractions C6I and C7I were partially soluble under test conditions.

Keywords
asphaltenes; maltenes; solubility

Introduction
Asphaltenes and maltenes are classified according to their solubility. If the solute “asphaltenes” and solvent “maltenes” are compatible, asphaltenes are considered to be stable in maltenes.[1]
Several studies have characterized differences between asphaltenes and maltenes.[2-4] The asphaltenes chemical characterization is generally carried out through techniques of elemental analysis to determine C, H, N and S composition, plasma-induced mass spectrometry to determine Ni, Fe and V levels and infrared spectrometry to characterize functional groups. These techniques do not directly investigate the colloidal properties of the asphaltenes, even with the relevant information obtained.[5]
The complexity of asphaltenes and their possible interactions with other species present in crude oil affect their solubility.[2] Variations in temperature, pressure and oil composition conditions during production are the main factors that cause flocculation and asphaltenes precipitation.[6-7]
Asphaltenes fractions can be extracted from petroleum according to the flocculant used in the extraction process, for example C7I fraction is obtained when n-heptane is used.[8,9]
The objective of this study was to assess the asphaltenes solubility in maltenes evaluating asphaltenes fractions C3I, C6I and C7I extracted from a crude oil sample with maltenes isolated in the C3I extraction process. In this way, is possible to interpret the asphaltenes solubility in maltenes as function of the asphaltenes fraction.

Methodology
Extraction of asphaltenes fractions
The extraction of the asphaltenes fractions insoluble in n-hexane (C6I) e n-heptane (C7I) from a Brazilian petroleum sample (13.83 °API at 15 °C and 0.9723 g/cm^3) was carried out following an adaptation of IP-143/78 standard method.[10] First, 30 g of oil was added to 1 L of flocculating agent, kept for 24h stirring and filtered under vacuum. Resins coprecipitated with the asphaltenes were removed in a Soxhlet extractor containing 1 L of flocculation agent. The solid residue was then dissolved in the Soxhlet extractor with 500 mL of toluene, the solvent was totally removed and finally obtained the dry asphaltenes fraction. The asphaltenes fraction insoluble in propane (C3I) was extracted with a petroleum:propane ratio of 1:10 (v/v) in a high-pressure system (40 bar) at high temperature (70°C).[8]
Solubility of asphaltenes fractions in maltenes
The solubility of the asphaltenes fractions C3I, C6I and C7I was evaluated at room temperature and 60 °C at 5.0% (wt/v) in the maltenes fraction. These tests were carried out adding maltenes on the asphaltenes with manual stirring for 10 min. and with magnetic stirring for 60 min.

Results and Discussion

In the tests to evaluate the effect of adding maltenes on the asphaltenes at room temperature and rest for 60 min, the asphaltenes fractions weren't fully soluble. The asphaltenes fractions solubility order was C3I > C6I > C7I, as expected. On the other hand, at 60 °C for 60 min, C3I fraction was completely soluble and C6I and C7I fractions were still partially soluble, as presented in Fig. (1).

Figure 1. Asphaltenes fractions C3I (a), C6I (b) and C7I (c) in maltenes (5% wt/v) after removal fluid part and rest for 60 min/60 °C.

The evaluation with addition of the maltenes and subsequent addition of the asphaltenes fraction with a magnetic stirring was carried out to improve homogenization and facilitate the solubilization of the solid fraction into the viscous liquid fraction. Under ambient conditions no solubilization was observed for the asphaltenes fractions. At 60 °C the asphaltenes fraction C3I became completely soluble and C6I and C7I were partially soluble, and also more soluble than respective tests with manual stirring.

The darker color and the appearance of the asphaltenes fraction/maltenes mixtures presented in Fig. (2a), (2b) and (2c) when compared to Fig. (2d) indicates solubilization of asphaltenes fractions in pure maltenes, in different extension. The C3I fraction in maltenes presented homogeneous aspect while the mixtures with C6I and C7I were partially soluble presenting solid particles visually adhered to the flasks.

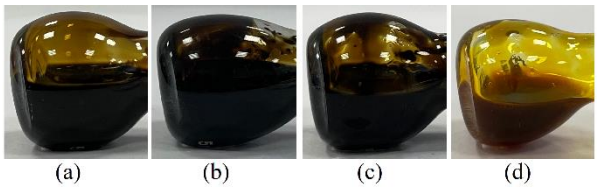

Figure 2. Asphaltenes fractions C3I (a), C6I (b) and C7I (c) in maltenes (5% wt/v) and pure maltenes (d) after rest for 60 min/60 °C.

Considering that asphaltenes fraction C3I was soluble in the maltenes fraction, it is possible to propose that asphaltenes fractions would have been soluble in maltenes with non-precipitated asphaltenes fraction, containing lower polarity molecules.

Conclusions

The complete solubilization of the asphaltenes fraction C3I in the maltenes extracted from a heavy petroleum sample was achieved with magnetic stirring at 60 °C for 60 min. Under ambient conditions this solubility behavior was not observed. The fractions C6I and C7I were partially soluble in all test conditions evaluated.

Studies on the solubility of asphaltenes fractions in maltenes contribute to avoid and mitigate problems related to deposition of asphaltenes in the processes of the oil industry.

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Responsibility Notice

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