Rio de Janeiro, Brazil, November 15 - 18 2022



# Effects of different solvents on the physicochemical properties of asphalthenic fractions

lago Oliveira<sup>1</sup>\*, Elton Franceschi<sup>1</sup>, André Poloni<sup>1</sup>, Larissa Gomes<sup>1</sup>, Gustavo Borges<sup>1</sup>, Flávio Albuquerque<sup>2</sup>, Cláudio Dariva<sup>1</sup>

<sup>1</sup>Center for Studies on Colloidal Systems (NUESC)/Institute of Technology and Research (ITP)/PEP/PBI/ Tiradentes University (UNIT), Aracaju, SE, Brazil. \*iagofilipe000@gmail.com <sup>2</sup>Petrobras, Centro de Pesquisas e Desenvolvimento Leopoldo A, Miguez de Mello (CENPES), Pio de

<sup>2</sup>Petrobras, Centro de Pesquisas e Desenvolvimento Leopoldo A. Miguez de Mello (CENPES), Rio de Janeiro, RJ, Brazil.

# Abstract

It is recognized that asphaltenes tends to aggregation and precipitation. Even at low concentrations they can adsorb at interfaces/surfaces, where each type of interaction plays an important role in different stages of oil production. To evaluate the behavior of asphaltenes, it is necessary to conduct studies that allow understand their physicochemical, as well how they behave interfacially and superficially. By using the Pendant Drop Tensiometry and Atomic Force Microscopy techniques, the present work aims to characterize the interfacial behavior and the surface structure of asphalthenic fractions obtained through the precipitation using Heptane, Propane and Carbon Dioxide as flocculant agents.

# Keywords

Crude Oil; Asphalthenic Fraction; Solvents.

### Introduction

Asphaltenes are known by their solubility and not by a well-defined chemical structure, they are insoluble in n-alkanes (such as Heptane), but soluble in aromatic hydrocarbons (such as Toluene) [1-2]. In addition, asphaltenes can also be dissolved in other solvents with high surface tension, such as pyridine, carbon disulfide and carbon tetrachloride, among others [3].

Asphaltenes make up the most aromatic and heaviest fraction of crude oil. They tend to aggregate and precipitate, since precipitation is dependent on chemical composition, temperature and pressure and these factors change according to the oil is raised from the reservoir to the surface [4]. Due to Asphaltenes complexity, understanding they properties becomes difficult.

To get around the problems caused by asphaltenes, solvents are used, for example, to reduce the viscosity of the oil and break up the emulsions. The use of different solvents for deasphalting can lead to different behaviors in these fractions, which is due to differences in the intermolecular interaction energy of the solvent molecules and the proximity of this energy to the intermolecular interaction energy of the asphaltenes [5].

In this scenario, the present work aims to collaborate with studies of characterization of asphalthenic fractions. The main goal is to obtain different fractions of two Brazilian crude oils (Oil 1 and Oil 2) and identify characteristics that can contribute to the understanding of the physicochemical behavior affected by the use of different solvents and how this affects the processes of deposition in a surface and their interfacial activity. Thus, asphalthenic fractions were obtained using four solvents, heptane, propane, and the equivolumetric mixture of Heptane/CO<sub>2</sub> and Propane/CO<sub>2</sub>.

## Methodology

Both oils used in this work were provided by Petrobras S.A. The main characteristics of these oils are summarized in Tab. 1.

Table 1. Crude oil properties investigated.		
Crude oil properties	Oil 1	Oil 2
°API (15 °C)	28.6 (±0.1)	27.4 (±0.1)
Viscosity 20 °C (mm <sup>2</sup> s <sup>-1</sup> )	62.0 (±4.3)	43.8 (±1.2)
Water content (%)	0.49 (±0.04)	0.97 (±0.02)
SARA Analysis (%)		
Saturated	49.4	45.9
Aromatics	33.1	22.6
Resins	17.0	21.0
Asphaltenes	0.6	3.3

The process of obtaining heptane-insoluble asphalthenic fractions was adapted from ASTM D6560-17 standard - IP 143/01 designation [6] and consists in the solubility of the crude oil in heptane (1 g of oil in 40 ml of Heptane), followed through stages of agitation, rest, filtration, collection and drying. The experimental procedure for the precipitation of insoluble fractions in propane consisted of adding approximately 25 ml of crude

oil and 200 ml of propane inside the variable volume cell (Approximately 10 Bar at room temperature), and then going through stages of agitation, rest, collection and drying. The experimental procedures are detailed in the work published by Oliveira et al. [7].

The asphalthenic fractions obtained in the presence of  $CO_2$  were obtained in a precipitation process like the one carried out with propane; however, the variable volume cell has a total volume of 18.5 mL. Approximately 1.7 ml of oil and 17 ml of a mixture with 8.5 ml of  $CO_2$  and 8.5 ml of a co-solvent (propane or heptane) were used. Four washing processes were carried out to maintain the volumetric proportions between oil and precipitating agent than those of the previous extractions (1/40 m/v). The operating pressure of the extraction was 150 bar and the temperature of 70 °C defined according with a subsequent study where it was possible to observe the precipitation of asphaltenes [8].

Some characterizations as fallows Fourier Transform Infrared Spectroscopy (FTIR), Elemental Analysis (CHN), Hydrogen and Carbon Nuclear Magnetic Resonance (NMR), Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) were carried out to obtain physicochemical characteristics of the fractions.

The surface characterization of the asphalthenic fractions were determined using the Atomic Force Microscopy (AFM) technique. Solutions of the fractions in toluene were prepared at a concentration of 1000 mg.L<sup>-1</sup> and deposited on glass substrates submerged in the solution.

The interfacial properties were determined by the pendant drop technique using static tests to obtain the interfacial tension as a function of time. The properties were determined at 25 °C. Ultra-pure MilliQ water was the aqueous phase and a solution of the asphalthenic fractions (without the presence of  $CO_2$ ), at different concentrations (from 10 to 3000 mg.L<sup>-1</sup>), in toluene represented the oil phase.

#### **Results and Discussion** Physicochemical characterizations

The FTIR spectra of the fractions showed a similar behavior of groups present with bands consistent with the expected composition for asphalthenic fractions [9-10], only undergoing changes in the intensity of the bands. In general, the fractions obtained with Oil 1 showed more intense aliphatic groups compared to Oil 2 which showed more aromatic groups. The fractions obtained with propane showed more heteroatoms in their composition. From the results of the elemental analysis, it was possible to suggest structural differences in the samples based on their H/C ratio, which is closely linked to the aromaticity of each fraction, in which the precipitated fractions of Oil 1 showed a behave more aliphatic and from Oil 2 more aromatic. This trend was also confirmed by NMR analyses. From the TG analysis, a greater thermal stability was observed in the samples obtained from Oil 1.

When the effects of this solvents were evaluated independent of the oil, it was concluded that the fractions obtained with heptane presented a greater aromaticity, both in the presence and in the absence of  $CO_2$ , and the fractions obtained with propane presented a more aliphatic behavior in addition to a greater presence of heteroatoms. The fractions obtained with propane+CO<sub>2</sub> were the most aliphatic among all fractions.

#### Characterization of surface arrangements

Figures 1 present the topographic images obtained by the AFM of the films from the asphalthenic fractions extracted with heptane and propane, as well as in the conditions in the presence of CO<sub>2</sub>.



Figure 1. AFM images of the fractions obtained with Heptane (AH), Propane (AP), Heptane +  $CO_2$  (ACH) and Propane +  $CO_2$  (ACP) of Oils 1 and 2 at a concentration of 1000 mg L<sup>-1</sup>, precipitated on the substrates in solution.

From the AFM images it can be observed that through the deposition methodology in solution, the asphalthenic fractions did not produce a homogeneous layer, but rather form aggregates, in which case the deposition occurs in overlaps. The same behavior was observed by BALABIN et al. [11], SYUNYAEV et al. [12] and OLIVEIRA et al. [7] on different surfaces analyzed, and this behavior corresponds to the aggregation tendency of asphaltenes.

By analyzing the arithmetic mean of the roughness (Ra) and the maximum height (Rz) obtained from each precipitated fraction, it can be observed the level of aggregation of the precipitated fractions on the substrates in solution.

When evaluating the different oils used, larger aggregates were present in the substrates in contact with the precipitated fractions of Oil 2, a behavior observed in all fractions regardless of the solvent used. Such behavior may be an indicative

of more pronounced intermolecular forces between the fractions, thus allowing a greater aggregation between the compounds present in the fractions (stronger interactions) of Oil 2. Such behavior may be related to the physical-chemical differences already evidenced between the fractions of oil 1 and oil 2 observed thorough the physicochemical characterizations presented above. These finds agree with the results observed by Oliveira et al. [7], in which asphalthenic fractions with a more aromatic behavior showed a greater capacity for self-association, generating higher and rougher precipitated films.

About the effects of the solvents used in the precipitations, it can observe values of roughness and maximum height of the film more evident in fractions precipitated with heptane in relation to the others. This may be an indication of a high aggregation capacity in these fractions. The same behavior was observed on the effect of solvents in both oils, showing a reduction in roughness and height from heptane to propane. By observing the effect of CO<sub>2</sub> in the systems, it can be highlighted visually the films showed that а more homogeneous behavior of aggregates distribution when compared to the fractions obtained without CO<sub>2</sub>. Also, lower height and roughness values were obtained for almost all situations.

#### Characterization of interfacial films

Figures 2 and 3 show the behavior of the interfacial tension over time for the insoluble fractions in heptane (AH1 and AH2) and propane (AP1 and AP2) of the oils selected in the studies.

It was possible to observe in systems above 10 mg  $L^{-1}$  a rapid drop in the interfacial tension in the initial minutes of the tests and, later, a smaller variation with time. This is an effect related to the migration steps of asphaltenes molecules to oil-water interfaces [7,13–16].

An increase in the asphalthenic fraction concentration in the system indicated that for the systems with the highest fraction concentration, the migration and interfacial adsorption processes are intensified, causing a more evident tension drop when compared to systems at lower concentrations [7,13,15].

Such behavior may be related to the solubility of the fractions in the solvent, since the asphalthenic fractions, composed mostly of asphaltenes, have toluene as a good solvent and the forces of interaction between fraction/solvent are strong. Thus, for systems with low concentration, there is a smaller process of interaction between the fractions and greater between the fractions and the solvent. This balance of interactions can influence the interfacial activity of the molecules, since this activity can be inversely related to the solubility, by the variation of the attractive potential between the structural heteroatoms of the fraction and the water [17]. Such behavior can serve as an indicator of the interaction forces between the same fractions.



Figure 2. Dynamic interfacial tension of Oil 1 asphalthenic fractions at different concentrations in toluene at 25° C. Heptane (a); Propane (b).



Figure 3. Dynamic interfacial tension of Oil 2 asphalthenic fractions at different concentrations in toluene at 25° C. Heptane (a); Propane (b).

Figure 4 shows the effect of solvents used to obtain the fractions in the equilibrium interfacial tension. The greater the adsorption of surfactants at the interface, the lower the interfacial tension. It can be observed that the fraction obtained with heptane showed a greater migration to the water/oil interface compared to that obtained with propane, evidencing a more pronounced activity interface in these fractions. It is worth mentioning that the fractions obtained with heptane showed greater aromaticity compared to those obtained with propane.

As observed when evaluating the concentration, such behavior can serve as an indication of the functioning of the forces of interaction between the same fractions. Since, despite being analyzed in the same model oil system (toluene), the fractions obtained with heptane may present stronger interaction forces when compared to the ones obtained with propane.



Figure 4. Interfacial tension effect by fraction concentration obtained from Oil 1 and Oil 2, with heptane (AH1, AH2) and propane (AP1, AP2).

Such results may related the be to physicochemical characteristics of the fractions, which suggest that the ones obtained with heptane generally presented a lower presence of heteroatoms (such as S, N and O) and a greater amount of unsaturation and aromatic groups in comparison with the fraction obtained with propane [7,17]. Such behavior may be related to the characteristics of the precipitating agents used and their different forms of interaction with the components of the crude oil used in the precipitation.

To observe the effect of the type of oil origin of the fractions on the interfacial activity, Fig. 5 presents a comparison between the interfacial tension curves by time for fractions insoluble in heptane and propane of Oils 1 and 2. Oil 1 showed a higher interfacial activity compared to Oil 2, regardless of the type of methodology used to obtain the fractions. In general, fractions of Oil 1 present a more pronounced initial tension drop, probably related to the lower acidic/polyaromatic character when compared with Oil 2, as well as to the lower presence of heavier fractions as evidenced by the SARA analysis. It also should be considered that the fractions were dissolved in toluene and, therefore, the more aromatic samples (Oil 2) would tend to have a greater affinity with the bulk medium and, therefore, a lower interfacial activity than those obtained from Oil 1.



Figure 5. Dynamic interfacial tension of fractions obtained with Heptane (AH1 and AH2) and Propane (AP1 and AP2) of Oils 1 and 2 in toluene at concentration of 1000 mg L<sup>-1</sup> at 25° C.

#### Conclusions

On this work it was possible to check the effect of different solvents on physicochemical properties of asphalthenic fractions. Accordingly with the type of solvent, the fraction can change they molecular arrangement, and this can affect, for example, the way the fractions are arranged superficially and interfacially.

As for the surface arrangement of the fractions, it was highlighted how the different solvents affect the structure, such as surface roughness and height of the agglomerates on a substrate. Higher values were found for the fractions obtained with heptane in relation to propane, both in the presence and absence of CO<sub>2</sub>. In general, the fractions obtained with heptane showed greater migration of surfactant/amphiphilic molecules to the water/oil interface in relation to those obtained with propane.

#### Acknowledgments

The authors thank Petrobras S.A., CAPES -Finance Code 001, CNPq and ANP (Agência Nacional do Petróleo, Gás Natural e Biocombustíveis) for financial support and scholarships.

## **Responsibility Notice**

The authors are the only ones responsible for the paper content.

#### References

- [1] Lei, Y. et al. ACS Omega 6, 1497–1504, 2021.
- [2] Nascimento, F. P. et al. Fuel 284, 118968, 2021.
- [3] Zuo, P., Qu, S. & Shen, W. J. Energy Chem. 34, 186– 207, 2018.
- [4] Sjöblom, J., Simon, S. & Xu, Z. Adv. Colloid Interface Sci. 218, 1–16, 2015.
- [5] Ilyin, S. O., Ignatenko, V. Y., Kostyuk, A. V., Levin, I. S. & Bondarenko, G. N. J. Pet. Sci. Eng. 208, 109329, 2022.
- [6] ASTM International. ASTM D6560-12. Pet. Prod. Lubr. Foss. Fuels 1–6, 2013.
- [7] Oliveira, I. et al. Energy & Fuels 32, 12174–12186, 2018.
- [8] Cruz, A. A. et al. The Journal of Supercritical Fluids 143, 24–31, 2019.
- [9] HONSE, S. O. et al. Quimica Nova, v. 35, n. 10, p. 1991–1994, 2012.
- [10] PÉREZ-HERNÁNDEZ, R. et al. Fuel, v. 82, n. 8, p. 977–982, 2003.
- [11] Balabin, R. M. et al. Energy and Fuels 25, 189–196, 2011.
- [12] SYUNYAEV, R. Z. et al. Energy & Fuels, v. 23, n. 3, p. 1230-1236, 2009.
- [13] Horváth-Szabó, G., Masliyah, J. H., Elliott, J. A. W., Yarranton, H. W. & Czarnecki, J. J. Colloid Interface Sci. 283, 5–17, 2005.
- [14] SZTUKOWSKI, Danuta M.; YARRANTON, Harvey
  W. Langmuir, v. 21, n. 25, p. 11651-11658, 2005.
- [15] Morais, W. J. S. et al. Energy and Fuels 31, 10233– 10244, 2017.
- [16] Alves, D. R. et al. Fuel 118, 21–26, 2014.
- [17] Yarranton, H. W., Alboudwarej, hussein & Jakher, R. Industrial Eng. Chem. Res. 39, 2916–2924, 2000.