



Isolation of Interfacially Active Molecules from Brazilian Oils and Characterization by High Resolution Analytical Techniques

Wanderson Romão^{1,2}, Eliane V. Barros^{1,2}, Natã C. L. Madeira¹, Luiz S. Chinelatto Jr.^{3*}, Marcia C. K. de Oliveira³, Valdemar Lacerda Jr.¹

¹Chemistry Department, Universidade Federal do Espírito Santo, ES, Brazil;

²Federal Institute of Education, Science and Technology of Espírito Santo, ES, Brazil;

³Research and Development Center CENPES/PETROBRAS, RJ, Brazil;

*email: lsilvino@petrobras.com.br

Abstract

Petroleum molecules with interfacial activity play a fundamental role in stabilizing water-in-crude oil emulsions (W/O) leading to significant flow assurance challenges during oil production and thus have been the focus of many studies. Using the wet silica method, three crude oils from Brazilian fields were fractionated into two fractions: one with the interfacially active molecules (IM) and another containing the non-interfacially active molecules, named clean up (CU) fraction, containing the non-adsorbed molecules onto silica during the wet silica method. Nuclear Magnetic Resonance (NMR) provided the average molecular parameters of the oils such as average linear chain length, bridgehead carbons and aromatic hydrogens. The characterization of IMs, CUs and their parent oil by high resolution and precision mass spectrometry (FT-ICR MS) showed the influence of Total Acid Number (TAN) in % of class O₂[H] found, but no clear differences were found between chemical composition of the IMs isolated. The IMs were rich in O₃S[H] class, with presumably natural origin.

Keywords

water-in-crude oil emulsions; interfacially active molecules; ESI(±)FT-ICR MS.

Introduction

In exploration of petroleum resources, a considerable amount of water is inevitable produced, leading to formation of W/O and severe production losses. Effective ways to treat W/O need a deep knowledge of the chemical structure of molecules responsible for stabilizing them. The results of many studies suggest that constituents of crude oil, such as resins, naphthenic acids, and asphaltenes, are the main components of crude oil responsible for the formation of robust interfacial films that stabilize W/O [1-3]. Due to the complexity and variety of different crude oils, much research is still necessary to identify the chemical structure of the IM to allow structure properties correlation and advances in optimum petroleum production. In this study, the wet silica method was applied for the isolation of IM of three crude oil samples from Brazilian fields to realize their crucial role in crude oil emulsion stability [4].

Methodology

Materials

Crude oil samples were supplied by PETROBRAS. Reagent grade toluene, methanol, n-heptane, formic acid and ammonium hydroxide were

purchased from Vetec Química Fina Ltd., Rio de Janeiro, Brazil. Chromium-(III) acetylacetonate (~98%), arginine (≥98), carbon disulfide (≥99.9), and C₂Cl₄ (≥99%); were obtained from Sigma-Aldrich-Merck. Chloroform-D (D, 99.8%) was obtained from Cambridge Isotope Laboratories. All chemicals were used without further purification.

Methods

SARA Analyses. The separation of the saturates, aromatic, resins, and asphaltenes fractions (SARA Analyses) was carried out using a modified version of the thin layer chromatography-flame ionization detection (TLC-FID) method. In this procedure, asphaltenes were separated and quantified by the ASTM D6560-17 standard procedure. Another portion of the same petroleum sample was separated by microdistillation into a <260 °C fraction and a >260 °C fraction. Supercritical fluid chromatography using carbon disulfide separated the <260 °C fraction into saturates (S1) and aromatics (A1). Complementary, the >260 °C fraction was fractionated by TLC-FID into the heavier saturates (S2), aromatics (A2), and the polar compounds (P). S1+S2 corresponded to the saturates, A1+A2 to the aromatics, and the polar compounds minus the asphaltenes to the resins.

NMR Measurements. Solution-state ^{13}C NMR spectra were recorded at 9.40 T on an Agilent 400 NMR spectrometer, operating at 100.44 MHz, using a 10mm probe. Samples were dissolved at 20 wt % in 0.05 M chromium(III) acetylacetonate (as the relaxation agent) in chloroform-D (CDCl_3). The following experimental conditions were used: 25.0 kHz spectral width, 10.2 μs (90°) rf pulses, 1.3 s acquisition time, 7 s pulse delay, and 5000 scans were accumulated. The nuclear Overhauser enhancement was suppressed by operating the spectrometer in the “inverse-gating” mode where the broad band proton decoupling was turned on only during acquisition periods. Solution state ^1H NMR spectra were recorded at 11.75 T on a Bruker Avance III 500 spectrometer, operating at 500.18 MHz, using a 5mm probe. Samples were dissolved at 5 wt % in $\text{CDCl}_3:\text{C}_2\text{Cl}_4$ 1:1 v/v. The following experimental conditions were used: 10.0 kHz spectral width, 3.3 μs (30°) rf pulses, 2.3 s acquisition time, 1 s pulse delay, and 128 scans were accumulated. All experiments (^1H and ^{13}C) were performed at 32°C .

ESI(\pm)FT-ICR MS. The samples of crude oil and the fractions were analyzed by mass spectrometry using a 9.4 T Q-FT-ICR MS hybrid device (Solarix, Bruker Daltonics, Bremen, Germany) equipped with a commercially available ESI source (Bruker Daltonics). The dynamic operating range for ion acquisition in the ICR cell was configured to m/z 200-1500. All samples were diluted to approximately 1.5 mg/mL in toluene/methanol 1:1 (v/v) solution containing 0.1% (v/v) formic acid and ammonium hydroxide for analysis in ESI(+) and ESI(-) modes, respectively. Each solution was injected by direct infusion at a flow of 5 $\mu\text{L}/\text{min}$. Each spectrum was acquired based on 200 scans with a time domain of 4 M (mega-points). Before acquisition, the device was externally calibrated with a solution of 0.1 mg/mL arginine (m/z 200-1500) in both ionization modes. The resolution powers were $m/\Delta m_{50\%} = 483,000\text{-}507,000$ for ESI (+) and $m/\Delta m_{50\%} = 382,000\text{-}505,000$ for ESI (-) (where $\Delta m_{50\%}$ is the total width of the peak at the midpoint of its maximum height at m/z 400), and the mass error was <1 ppm. These settings provided the attributions for unequivocal molecular formula for individually charged molecular ions. The mass spectra were processed using an algorithm developed specifically for processing of the signals: Composer software package [5]. The data from spectra were calibrated, and the elemental composition was determined by measuring the values of m/z . The results were expressed in a graph of class distribution of heteroatomic compounds and graph of DBE (double bond equivalents and rings) vs the number of carbon atoms for better visualization and interpretation of the MS results. The level of unsaturation of each compound can be deduced from Eq. (1), where the higher the value of DBE is, the greater the hydrogen deficiency of the compound:

$$\text{DBE} = \text{C} - (\text{H}/2) + (\text{N}/2) + 1 \quad (1)$$

where C, H, and N are the numbers of carbon, hydrogen, and nitrogen atoms present in the molecule, respectively. The M_w values are provided by the Composer software processing and obey the following formula in Eq. (2):

$$M_w = \sum_i (N_i M_i^2) / \sum_i (N_i M_i) \quad (2)$$

where, M_w is the average weight molar mass obtained from the mass spectra, M_i is the m/z value of peak i and N_i is the peak intensity [6].

Results and Discussion

Crude oil assay

Table 1 summarizes crude oils characterization.

Properties\OILs	OIL1	OIL2	OIL3
TAN			
(mg of KOH/g of oil)	1.09	0.40	1.10
ASTM D664-18			
Density at 20°C	0.8992	0.8830	0.9174
($\text{g}\cdot\text{cm}^{-3}$)			
$^\circ\text{API}$ at 15.6°C	25.1	27.9	22.0
ISO 12185			
Saturates (wt%)	58.3	59.7	49.8
Aromatics (wt%)	23.4	21.5	29.2
Resins (wt%)	18.0	18.7	19.6
Asphaltenes (wt%)	<0.5	<0.5	1.4
ASTM D6560-17			
(0.3)	(0.1)		
Water (vol%)			
ASTM D4377-20	0.79	0.20	1.11

NMR characterization

NMR data for the oils are summarized in Table 2.

*Symbol	OIL1	OIL2	OIL3
Hdar	2.3	2.0	2.9
Hmar	2.3	1.7	2.6
Har	4.6	3.8	5.5
Holf	<0.1	<0.1	<0.1
Halfa	8.6	7.5	10.6
H β -1	14.1	12.8	14.8
H β -2	43.3	48.0	40.8
H γ	29.2	27.8	28.1
Hsat	95.3	96.1	94.4
Car-alk	6.2	4.8	7.4
Car-H	8.3	6.9	9.7
Car-b (Car-ar + Car-ar-ar + Car-Me)	4.1	3.7	5.1
Car tot	19.6	16.7	23.4
Csat	80.4	83.3	76.6
Cmet-term	4.1	4.8	3.7
Cmet-bran	8.4	7.0	8.5
Average linear chain length (in carbon atoms)	12	14	11

*Symbols according to reference [7].

According to the Brazilian petroleum regulatory agency “Agência Nacional do Petróleo, Gás Natural e Bicombustíveis”, oil 3 with API gravity 22.0 (see Table 1) is classified as heavy and oils 1 and 2 are medium. Oil 3 has the highest asphaltene content and oils 1 and 3 have higher TAN values. Oil 1 has a higher degree of bridgehead carbons (Car-b), as expected for its higher degree of aromatics and asphaltenes (see Table 2). In the aliphatic region of the ^1H NMR spectra, $\text{H}\beta\text{-2}$ is higher than $\text{H}\beta\text{-1}$ for all samples. This is an indication that paraffinic hydrogens in long alkyl chains attached to aromatic rings are higher than naphthenic hydrogens and paraffinic hydrogens in short alkyl chains attached to aromatic rings.

ESI(\pm)FT-ICR MS characterization

Figure 1 displays the ESI(-)FT-ICR MS spectra of three crude oils. The profiles for all crude oils 2 and 3 were quite similar, with maxima at m/z 717 and 674 Da. Crude oil 1, for its turn, shows a maximum at 598 Da. The CU extracted compounds with lower molecular weight.

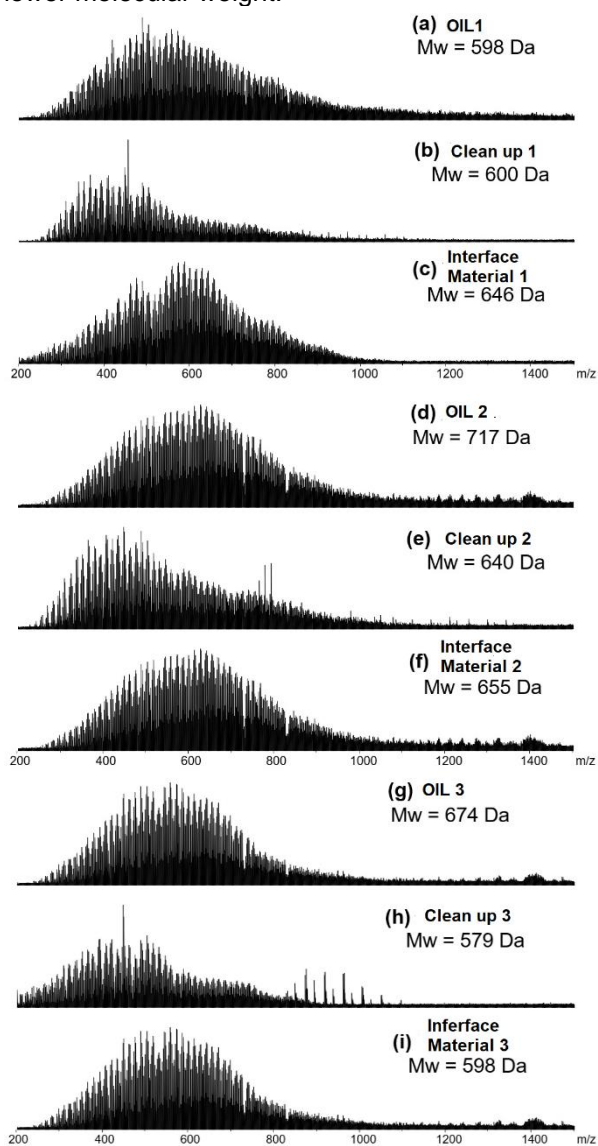


Figure 1. ESI(-)FT-ICR MS spectra of crude oils 1-3, their CUs and IMs.

Thus, the IM are concentrated in higher molecular weight polar compounds. The neutral N class found in ESI(-)FT-ICR MS spectra are abundant in the three oil samples and their respective CU fractions, while acidic $\text{O}_2[\text{H}]$ and mixed $\text{O}_3\text{S}[\text{H}]$ are the more abundant classes in the IM (see Figure 2). The most abundant $\text{O}_3\text{S}[\text{H}]$ species in IM have a continuum distribution from C_{14} to C_{24} with DBE from 1 to 5 with the most abundant structures $[\text{C}_{17}\text{H}_{28}\text{O}_3\text{S}-\text{H}]^{-1}$; $[\text{C}_{18}\text{H}_{30}\text{O}_3\text{S}-\text{H}]^{-1}$ and $[\text{C}_{19}\text{H}_{32}\text{O}_3\text{S}-\text{H}]^{-1}$ (DBE 4 in all cases) suggesting surfactants naturally present in petroleum likely thiophenic carboxylic acids. Anthropogenic chemical products such as surfactants artificially added to crude oils to alter wetting characteristics do not span such a wide range of carbon-number and DBE at the same time [8]. For instance, linear alkylbenzene sulfonates are the commercially and domestically widest-used surfactants in the detergent industry and have a discrete DBE of 4 [9]. Unsurprisingly, the class $\text{O}_2[\text{H}]$, presumably of carboxylic acids, was the most abundant class in oils 1 and 3, with higher TAN values (see Figure 2 and Table 1). But some non-interfacially active class $\text{O}_2[\text{H}]$ remains in the CUs. Although oil 2 has the lowest TAN value, its IM has a more abundant class $\text{O}_2[\text{H}]$ than in the parent oil.

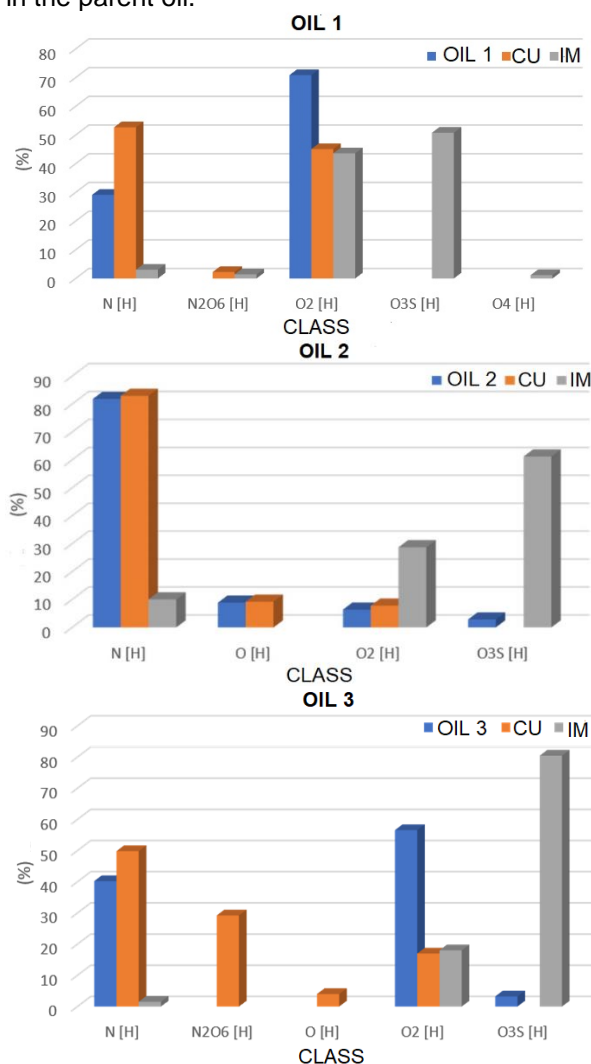


Figure 2. Class distribution obtained from ESI(-)FT-ICR MS data for crude oils 1-3, their CUs and IMs.

The relevant presence of class O₂[H] in the composition of these IMs confirms the participation of carboxylic acids in the stabilization of W/O for the studied oils. The class distribution obtained by ESI(+)-FT-ICR MS (Figure 3) reveals class N[H] as being the most abundant for in all the oils and its fractions, having pyridine as the basic structure forming its components. This profile of predominance of class N[H] when applying ESI(+)-FT-ICR MS is commonly observed in studies of crude oil due to the more efficient ionization of the pyridine compounds versus the other classes, resulting from the greater basicity of these compounds in solution. Only subtle differences were observed in the compositions of the crude oils and its fractions. Graphs of DBE vs carbon number for N[H] class plotted with data from ESI(+)-FT-ICR MS (data not shown) demonstrates a continuum distribution from C₃₀ to C₅₅ carbon atoms (maximum at C₄₂) with DBE from 7 to 15 (maximum at 9) for the three IMs suggesting the presence of aromatic rings. No clear correlations were found between chemical composition of the IMs determined by ESI(±)-FT-ICR MS (Figures 1 - 3), SARA analysis of crude oils (Table 1) and NMR data for the oils (Table 2).

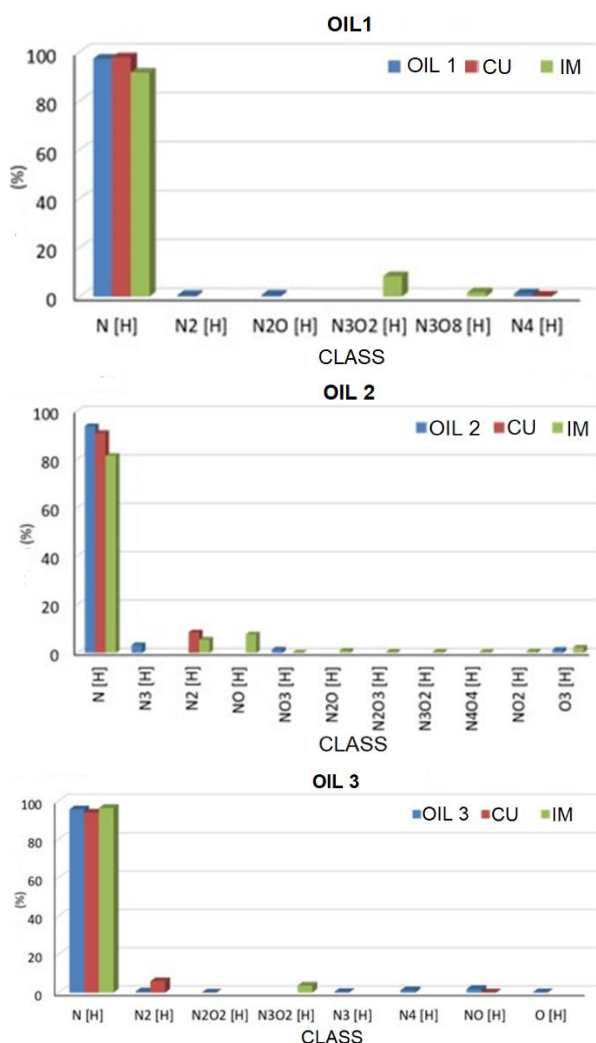


Figure 3. Class distribution obtained from ESI(+)-FT-ICR MS data for crude oils 1-3, their CU and IM.

Conclusions

The chemical characterization of IMs isolated from three different crude oils by the wet silica method evidenced their polar, aromatic and higher molecular weight hydrocarbon composition. These molecules are adsorbed onto the aqueous surface of the silica particles. CUs have predominant lower molecular weight hydrocarbon composition and contains the non-adsorbed molecules onto the aqueous surface of the silica particles. On the basis of the wet silica method, the sulfonate classes O₃S[H], with presumably endogenous origin, and O₂[H] have a surface-active character, because they are retained over aqueous media. N[H] class is abundant in the three oils, its CUs and IMs, probably due to the more efficient ionization of the pyridine compounds versus the other classes. The IMs are plenty of molecules crowded with heteroatoms having at least one pair of non-bonding valence shell electrons (i.e., N, O and S) suggesting hydrogen bonding may play an important role in stabilizing the w/o as already reported in the literature [10]. The characterization described in the present work may provide key information for developing new ways for the treatment of W/O, reducing or mitigating flow assurance issues.

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Responsibility Notice

The authors are the only responsible for the paper content.

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