



Comprehensive assessment of petroleum composition and interfacially active species to improve the understanding of water-in-oil emulsion stability

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Abstract

Emulsion stability can be controlled by the surfactant characteristics of crude oil constituents, such as asphaltenes, resins, and acid compounds. These components may generate a molecular layer at the water/oil interface, stabilizing the emulsion by resisting coalescence among the dispersed droplets. Thus, one of the fundamental objectives in oil production is to understand which species contribute to forming these stable emulsions and determine the best method to treat them. In this context, this work aimed to comprehensively characterize crude oils from four wells of the Campos Basin that produce emulsion and the species at their oil/water interface. Multiple analytical techniques were applied to assess the composition of the crude oils and the interfacially active species, which were isolated by the "wet silica" method at 66.6% water/g silica gel. The applied analytical techniques include conventional gas chromatography (GC), higher resolution two-dimensional gas chromatography (GC×GC), and Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). The results showed that low molecular weight monocarboxylic acid compounds containing sulfur and oxygen are mainly responsible for stabilizing water-in-oil emulsions under the evaluated conditions, increasing the viscosity of water-in-oil emulsion.

Keywords

Petroleum production; Stable emulsion; Oil/water interface; Comprehensive chemical analysis.

Introduction

The formation of stable emulsions is one of the most pressing problems in oil production from mature fields. Typically, water-in-oil (W/O) emulsions associated with oil production exhibit complex rheological behavior and a significant increase in viscosity relative to the viscosity of dehydrated oil.

The stability of the emulsions is directly tied to the presence of natural stabilizers in petroleum, such as resins, asphaltenes, fine solids (organic and inorganic), and acidic compounds like phenols and naphthenic acids [1, 2, 3]. Furthermore, the stability and viscosity of emulsions are intricately linked to the chemical composition and rheological properties of the crude oil and the volume fraction of the dispersed phase [4].

In this context, this work presents thorough research applying conventional and ultra-high-resolution analytical techniques commonly used in the petroleum industry and research to evaluate emulsions. These techniques, including gas

chromatography (GC), Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS), and two-dimensional gas chromatography (GC×GC), were employed to comprehensively assess the chemical composition of crude oils from mature fields of the Campos Basin and identify the interfacially active species isolated from them. Our goal is to provide a robust understanding of water-in-oil emulsion formation and stability.

Methodology

Samples

Four crude oil samples were collected in shallow water wells (up to 300 m) in the Campos Basin that produce oil with considerable water/oil emulsion formation. These samples underwent a step of dehydration before compositional analysis. Table 1 presents the sample codes and their physical-chemical properties.

Table 1. Physical-chemical properties of samples

Sample	BSW	API	TAN	Viscosity (Pa.s)	
				Oil	Emulsion W/O
C5P1	49	19.9	1.4	0.559	1.379
C5P2	62	20.4	1.4	1.165	2.034
C5P3	67	17.1	2.6	3.779	3.979
C6P1	41	24.7	0.5	1.703	1.703

BSW: Bottom sediment Water (ASTM D7829-13 (2018)); API: American Petroleum Institute (ASTM D1298-12b (2017)); TAN: Total Acid Number (ASTM D664-09); Viscosity (rheometer AR 1500ex, TA Instruments).

Crude Oil Characterization

In the SARA analysis, the crude oil samples were first fractionated into saturates (S), aromatics (A), resins (R), and asphaltenes (A). The total crude oils were also assessed by GC-FID and FT-ICR MS. See details of the analysis conditions in Lima et al., (2022) [5].

Extraction of Interfacial Material

The interfacially active species was separated from the emulsions according to the methodology developed by Jarvis et al., (2015) [6]. The solutions were prepared using 1 g of each oil sample, 20 mL of heptol (50:50 v/v heptane:toluene), and 1 g of previously prepared wet silica. Additionally, 10 mL of heptol was used to remove unretained compounds from the column (F1, CNR). Then, 10 mL of the MeOH:toluene mixture (10:25 v/v) was used to separate the interfacial active compounds (F2, IM). GCxGC-TOFMS assessed the IM fraction to identify the interfacial active species.

Results and Discussion

GC-FID and SARA

In the area of flow assurance, it is essential to chemically understand petroleum at a molecular level to evaluate its potential to form stable emulsions. In the assessment of the composition of the four crude oil samples by GC-FID (Fig. 1), a significant difference in the profile (gas chromatogram) is observed.

The C6P1 sample, for instance, showed a greater abundance of *n*-alkanes and lower UCM (unresolved complex mixture) among the studied oils, reflecting characteristics of a lighter and less biodegraded oil [7].

On the other hand, sample C5P3 presented a lower abundance of peaks resolved by GC-FID, which include linear, branched, and cyclic hydrocarbon compounds, pointing to its classification as heavy oil and very biodegraded.

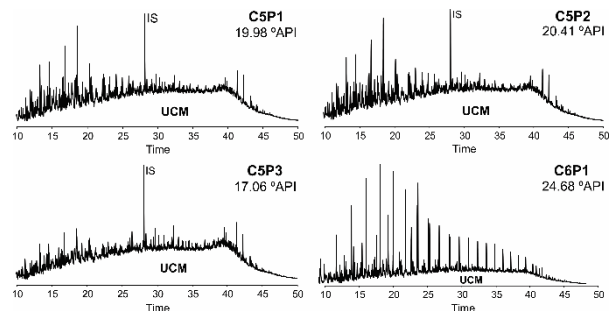


Figure 1. GC-FID chromatograms of the four oil samples from the Campos Basin. IS: internal standard (5 α -androstane); UCM: Unresolved Complex Mixture.

In addition, sample C5P3 stands out with the highest abundance of resins (25.61% m/m) and asphaltenes (22.70% m/m), with a consequent decrease in the R/A ratio (or increase in the A/R ratio), consistent with its classification in extra-heavy oil with very high acidity (2.6 TAN, Table 1). The high molar mass and size of these polar molecules contribute to this sample's increased viscosity and emulsion (Table 1), thereby enhancing its stability (higher resistance to emulsion breakage, either by centrifugation or by adding demulsifiers).

Furthermore, the ratios of resin and asphaltene over saturated and aromatic (R+A)/(S+A) (Fig. 2a) and resin and asphaltene over saturates (R+A)/S (Fig. 2b), proposed in this work, indicate that a higher content of polar compounds associated with a higher water content (BSW) can promote the stabilization of emulsions.

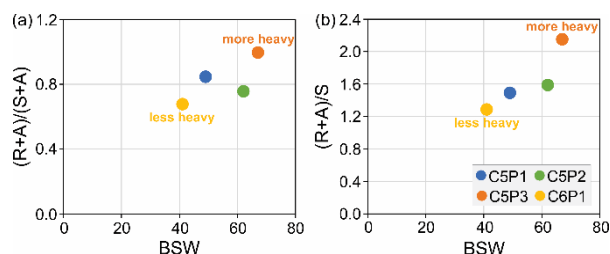


Figure 2. BSW versus the parameters based on SARA fractions (R+A)/(S+A) (a) and (R+A)/S (b) for the four oil samples from the Campos Basin.

FT-ICR MS

The FT-ICR MS analysis, a high-accuracy and mass-precision method, was conducted to determine the classes of polar compounds that have the most influence on emulsion stability (Fig. 3a).

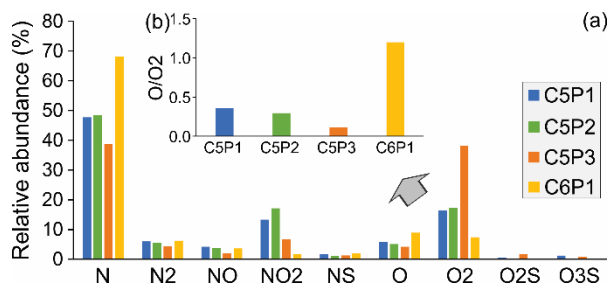


Figure 3. Heteroatomic class distribution with a relative abundance higher than 1% (a) and O/O₂ ratio (b) obtained from ESI(-) FT-ICR MS analyses of the four oil samples from the Campos Basin.

Oil sample C5P3 presented a considerably greater abundance of acidic compounds in the O₂ class (38.0%; Fig. 3a). The less heavy and biodegraded sample C6P1 presented the lowest percentage of compounds in this O₂ class (7.4%). In addition, the NO₂ class had a very low abundance (1.6%), and the O₂S and O₃S classes were not detected in this sample.

It was also observed that, considering the oil samples evaluated in this work, the O₂ class compounds (acids) were found to be more influential in the formation of stable emulsions than the O class compounds, as indicated by the lower O/O₂ ratio for the sample C5P3, contrary to the outcomes of Pereira et al. 2014 [2]. This underscores the importance of a comprehensive chemical analysis in understanding emulsion stability.

Additionally, a positive correlation between the percentage of the O₂ class (composed mainly of carboxylic acids) and the sum of the percentages of the O₂, NO₂, O₂S, and O₃S classes (mostly composed of compounds with carboxylic functional group) with TAN values (Fig. 4a and 4b) and BSW (Fig. 4c and 4d) was observed. As the carboxylic acids present in these classes are considered emulsifiers naturally found in crude oil [2, 3], the greater abundance of the O₂ class observed for the sample C5P3 can effectively contribute to a better stability of the emulsion generated from this oil.

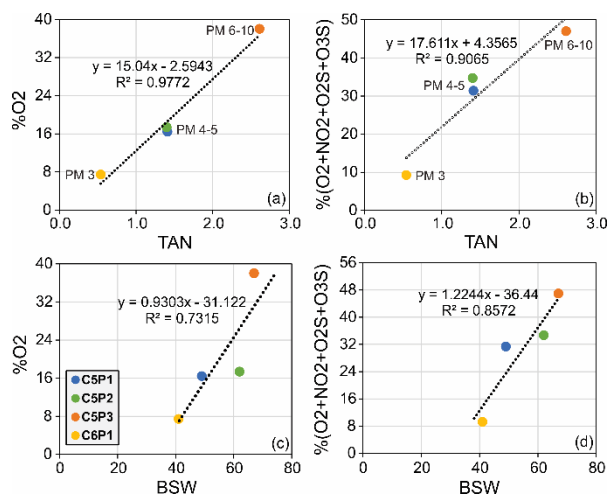


Figure 4. Correlation of TAN and BSW with the percentage of the O₂ class (a; c) and the sum of the

percentage of the O₂, NO₂, O₂S, and O₃S classes (two or more oxygens) (b; d).

Fig. (5) shows that the monocarboxylic acids in the O₂ class that potentially most contributed to the stability of the emulsions have DBE 3, 4, and 5, especially for sample C5P3.

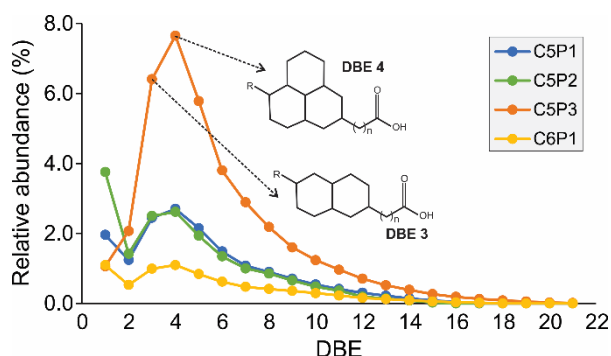


Figure 5. DBE distribution for the O₂ class obtained by ESI(-) FT-ICR MS analyses of the four oil samples from the Campos Basin.

GC×GC-TOFMS

The interfacially active species in the IM fraction were also analyzed by GC×GC-TOFMS. The highest total concentration for sample C5P3 can be seen in the Table 2, corroborating the data from previous analyses.

Table 2. Concentration (μg/g oil) of monocarboxylic acids in the analyzed interstitial materials

C ^a	¹ t _R (s) ^b	² t _R (s) ^c	Concentration (μg/g)			
			C5P1	C5P2	C5P3	C6P1
C6	490	1.21	n.d ^d	n.d.	4.2	0.3
C7	585	1.28	0.3	0.4	1.2	0.2
C8	715	1.40	1.6	1.8	3.2	1.2
C9	875	1.49	4.1	4.9	6.8	3.1
C10	1055	1.54	2.4	3.2	3.3	1.4
C11	1255	1.58	0.4	0.6	0.7	0.3
C12	1455	1.61	14.9	14.6	19.7	7.2
C13	1655	1.61	1.1	0.8	0.9	0.6
C14	1780	1.60	n.d.	n.d.	0.5	0.2
ram						
C14	1855	1.62	12.2	11.4	14.9	6.4
iso-C15	1975	1.61	0.8	0.7	0.7	0.3
ai-C15	1990	1.63	0.8	1.1	1.2	0.4
C15	2045	1.62	3.9	3.8	4.2	2.0
C16	2230	1.64	49.3	47.8	73.3	23.0
iso-C17	2300	1.61	0.4	0.8	1.7	0.2
ai-C17	2320	1.61	n.d.	n.d.	n.d.	>0.1
C17:1	2360	1.62	n.d.	n.d.	4.0	0.2
C17	2410	1.62	2.9	3.5	4.3	1.7
C18:1	2530	1.70	1.6	2.3	0.5	0.9
C18	2580	1.63	21.6	24.3	25.7	10.6
C19	2745	1.62	0.3	0.4	0.6	0.2
C20	2900	1.62	0.5	0.7	n.d.	0.3

C21	3055	1.62	0.3	0.2	n.d.	0.2
C22	3200	1.62	0.9	0.7	n.d.	0.6
C23	3345	1.61	0.2	n.d.	n.d.	0.2
C24	3485	1.61	0.3	n.d.	n.d.	0.1
Total	-	-	121.6	124.5	171.8	60.6

^aFirst-dimension retention time; ^bSecond-dimension retention time; not determined.

The presence of saturated, naphthenic, and aromatic hydrocarbons and monocarboxylic acids was observed, in addition to other compounds containing mainly Ox and OxSy groups, as previously observed by FT-ICR MS results. The predominance of low molecular weight monocarboxylic acids (naphthenic and aromatic) was observed, similar to the findings by Pauchard et al. [8].

Conclusions

The evaluation of four oils from Campos Basin (Brazil) focused on interfacially active species revealed the influence of monocarboxylic acid compounds to contribute to emulsion stability. Our study shows that the species with a positive influence on stability are especially aromatic and naphthenic acids, which were revealed by FT-ICR MS and confirmed by GC×GC-TOFMS.

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Responsibility Notice

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