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Waxy Crude Oil Emulsion Gel: Impact on Flow Assurance[†]

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In oilfield operations, the formation of crude oil emulsions is very common and can cause significant flow assurance problems during oil production. These emulsions can be very stable as a result of the presence of polar compounds, such as asphaltenes and resins, that play the role of natural surfactants and also because of the occurrence of many types of fine solids that can form resistant films at the crude oil/water interface. Gelled waxy crude oil flows have been largely studied, and the effect of dispersed water on crude oil rheology has been well-characterized; however, little attention has been given to the potential impact of waxy crude oil emulsion gel formation. In this study, it is shown that in some waxy crude oils the presence of water above a threshold value could promote gel formation, significantly changing the viscosity of the mixture. The rheological properties of waxy crude oils were determined at different water cuts, temperatures, and shear rates, and also a chemical characterization of these waxy crude oils was carried out. Highly stable and viscous emulsions with water cuts as high as 70% and wax—oil gel emulsions were observed. Rheological flow curves show viscosity values much higher than usually obtained for other waxy crude oils. Furthermore, strong shear-thinning behavior of the crude oils and emulsions at low-temperature conditions were seen as well.

1. Introduction

The formation of crude oil emulsion is mainly caused by high shear rates and zones of turbulence encountered at different points of production facilities, especially at the choke valve. These emulsions can be very stable as a result of the presence of polar compounds, such as asphaltenes and resins, that play the role of natural surfactants[1−3] and also because of the occurrence of many types of fine solids (e.g., clays and scales) that can form resistant films at the crude oil/water interface.[4−6] It is also widely known that emulsion increases fluid viscosity, depending upon the oil composition, water amount, and temperature.

Moreover, in the case of waxy crude oil multi-phase production in offshore environments, which is usually characterized by low ambient temperatures, it becomes important to evaluate the fluid rheology near the gel point of the crude oil emulsions.[11] In such cases, the viscosity can further increase by an order more, thus raising the flowing pressure drop.

The presence of paraffinic wax in crude oil is known to cause significant flow assurance problems related to wax deposit buildup and gel formation.[7−11,19] At low-temperature conditions, wax crystals nucleate in the bulk and form a solid crystalline network structure that changes the rheological behavior of the oil. Hence, in a waxy crude oil emulsion, the structure of a load-bearing gel captures the water droplets, which serve to promote the percolation condition necessary for a volume-spanning solid network. The presence of an emulsified water—oil interface contributes to the mechanical strength of a gel by providing bonding sites for the paraffin wax crystals. The interfacial tension associated with the water droplets may also impart mechanical strength to the gel structure. As an example of that, the presence of emulsified water effectively increases the pour point of waxy crude oils and its viscosity and may also exacerbate problems related to wax gelling.

The Brazilian Petroleum Company (Petrobras) has a pre-established technical specification for the flow assurance requirements at the selection phase of production development projects that include emulsion stability and oil and emulsion rheological tests. During these rheological tests of waxy crude oil samples, an unusual behavior has been observed. Because these data are used for selection and adjustment of the emulsion model for the simulation, some additional tests may be required to understand this new phenomenon.

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(1) Gafonova, O. V.; Yarranton, H. W. *J. Colloid Interface Sci.* **2001,** *241,* 469–478.
(2) Mclean, J. D.; Kilpatrick, P. K. *Colloids Surf., A* **2003,** *220,* 9–27.
(3) Yang, X.; Verruto, V. J.; Kilpatrick, P. K. *Energy Fuels* **2007,** *21,* 1343–1349.
(4) Yan, N.; Gray, M. R.; Masliyah, J. H. *Colloids Surf., A* **2001,** *193,* 97–107.
(5) Sullivan, A. P.; Kilpatrick, P. K. *Ind. Eng. Chem. Res.* **2002,** *41,* 3389–3804.
(6) Sztukowski, D. M.; Yarranton, H. W. *J. Colloid Interface Sci.* **2005,** *285,* 821–833.

(7) Kané, M.; Djabourov, M.; Volle, J. L.; Lechaire, J. P.; Frebourg, G. *Fuel* **2003,** *82,* 127–135.
(8) Venkatesan, R.; Östlund, J. A.; Chawla, H.; Wattana, P.; Nydén, M.; Fogler, S. *Energy Fuels* **2003,** *17,* 1630–1640.
(9) Tinsley, J. F.; Jahnke, J. P.; Heather, D. D.; Prud'home, R. K. *Energy Fuels* **2009,** *23,* 2056–2064.
(10) Paso, K.; Silset, A.; Sorland, G.; Gonçalves, M. A. L.; Sjöblom, J. *Energy Fuels* **2009,** *23,* 471–480.
(11) Visintin, R. F. G.; Lockhart, T. P.; Lapasin, R.; D'Antona, P. *J. Non-Newtonian Fluid Mech.* **2008,** *149,* 34–39.

In this study, it is shown that in some waxy crude oils the presence of water above a threshold value can increase the gel formation, significantly increasing the viscosity of the oil. The rheological properties of waxy crude oils were examined at different water cuts, temperatures, and shear rates, and also a chemical characterization of these waxy crude oils was carried out. Finally, a qualitative interpretation of the structure of waxy crude oil gels in the presence of water is proposed.

2. Experimental Section

2.1. Materials. Three Brazilian waxy crude oils, identified as A, B, and C, were selected for this study. The main properties of the oils are reported, where the values of physical–chemical properties can be considered typical of many waxy crude oils.

2.2. Basic Characterization of Crude Oils. A saturates, aromatics, resins, and asphaltenes (SARA) analysis was performed in a thin-layer chromatography–flame ionization detection (TLC–FID) system as reported in the literature.[12] The asphaltene content was determined by the IP143 method. The wax appearance temperature (WAT) determination was measured by differential scanning calorimetry (DSC)[13] in a temperature range from −40 to 100 °C. The total acid number (TAN) was determined accordingly to the American Society for Testing and Materials (ASTM) D664 method. The density value was obtained by the ISO12185 method. The water content of the crude oils was measured by coulombimetric Karl Fischer titration.

2.3. Emulsion Preparation and Stability. Water-in-oil emulsions were prepared using a synthetic brine consisting of 5.0 wt % NaCl in Milli-Q water, at aqueous volume fractions of 10, 30, 50, and 70%. The crude oils were thermally preconditioned in an oven at 60 °C for at least 1 h to redissolve any wax already precipitated, and after that, the aqueous phase was added. Emulsification was performed using an Ultra Turrax homogenizer at 8000 rpm for 3 min at 25 °C. Subsequently, bottle tests were performed at 60 °C to visually determine emulsion stability.

2.4. Rheological Analysis. Rheometric measurements were performed using a controlled-stress rheometer. Dynamic viscosity was measured using a concentric cylinder geometry, while the emulsion was cooled at a programmed cooling rate (1 °C/min) from the starting temperature (60 °C) to the hold temperature (4 °C). The range of shear rate applied was $20-250 \ s^{-1}$.

2.5. Droplet Size Distribution. The drop size distribution of the water–crude oil emulsion type was determined using the laser diffraction technique. The light produced when a laser beam passes through an emulsion is diffracted as a function of the particle size. The emulsion was diluted in spindle oil, and the droplet size distribution was determined considering the volume of droplets. The average diameter of the particles was determined as a function of the total volume of the droplets. The study was based on the comparison of the mean diameter characterizing 10, 50, and 90% of the total particles, respectively named $D(0.1)$, $D(0.5)$, and $D(0.9)$.

2.6. Chemical Analysis of Emulsionated Samples. Every sample was centrifuged of 10 000 rpm for 30 min at 25 °C. The nonresolved emulsion was dried until the weight remains constant (60 °C, under vacuum). A solid–liquid extraction with the Soxhlet procedure was conducted to separate the components, using hexane and toluene as solvents. The dried sample was first extracted with hexane (resulting in a hexane-soluble fraction), and the hexane-insoluble fraction was extracted with toluene (resulting in a toluene-soluble fraction). The organic-soluble fractions were dried, quantified, and analyzed by infrared spectroscopy.

(12) Jiang, C.; Larter, S. R.; Noke, K. J.; Snowdon, L. R. *Org. Geochem.* **2008,** *39,* 1210–1214.
(13) Gimzewski, E.; Audley, G. *Thermochim. Acta* **1993,** *214,* 149–155.

2.7. Isolation and Characterization of *n*-Paraffin in Crude Oil.
2.7.1. Separation of the Normal Paraffin from the Crude Oils (To Obtain Rich Fractions of n-Paraffins). A new methodology, developed with the aim of separating the *n*-paraffins from the crude oils was used. About 1 g of each crude oil was dissolved in iso-octane and percolated in a column packaged with activated alumina (30 cm of fix bed × 1 cm diameter) to eliminate the polar compounds (non-hydrocarbons). Then, a Soxhlet extraction was performed with the alumina impregnated with the polar compounds as the solid phase and the iso-octane used to percolate the column as the liquid phase, with the intention of recovering any apolar compounds (non-adsorbed fraction in alumina) that may have been adsorbed on the alumina. After the extraction, the fraction soluble in iso-octane was evaporated and a cold mixture (approximately −21 °C) of 22 mL of acetone and 7 mL of petroleum ether was added to approximately 500 mg of the residue of the fraction soluble in iso-octane (maltenes). The new mixture was sonicated for about 30 min and then cooled to −21 °C for 2 h in a thermal container with dry ice, as well as the whole Millipore apparatus to be used for filtration. Thereafter, a filtration under vacuum was carried out, and the precipitate obtained was washed with 500 mL of a cooled mixture of acetone and petroleum ether. The material soluble in the mixture of acetone and petroleum ether, called non-paraffins, was recovered by solvent evaporation. The fraction rich in *n*-paraffins, retained on the polytetrafluoroethylene (PTFE) 0.45 μm membrane, was recovered by washing the membrane with boiling iso-octane.

2.7.2. Characterization of the n-Paraffinic Fraction by Gas Chromatography. For the characterization of the *n*-paraffinic fraction, a new methodology was developed to determine the carbon number distribution using high-temperature gas chromatography (HTGC) and high-temperature simulated distillation (HTSD). For samples analysis, it was necessary to weigh 0.2 g of the sample and prepare a solution with 7.8 g of carbon disulfide (CS_2). The final concentration should be around 2% (in weight). Each sample was analyzed twice, once using HTSD and other using HTGC (carbon number distribution method). The two techniques were applied individually, using the same conditions of analysis. After the analyses, the results obtained for both analyses were compared and the complete composition of the sample was recalculated.

3. Results and Discussion

3.1. Rheological Behavior. Rheological properties of the waxy crude oils, such as viscosity, depending upon the temperature, shear rate, and water content, were measured. In general, with the addition of water to the crude oil, the viscosity of the sample increases 15 times for 70% water cut at 60 °C, as shown for the relative viscosity of crude oil A in the right panel of Figure 1. Relative viscosity (η_R) is the ratio between emulsion viscosity (η_E) and crude oil viscosity (η_o) (eq 1).

$$\eta_R = \frac{\eta_E}{\eta_o} \qquad (1)$$

In Figures 1, 3, and 5, the experimental data for each crude oil was plotted for each of the four emulsions, with different water content for each crude oil. The increase of the relative viscosity was greater at temperatures higher than the pour point, for the emulsions, and the viscosity increased with the water content. The main contribution of the viscoelastic properties of the emulsion is given by the dispersed phase.

Crude oil A exhibited Newtonian flow behavior, but crude oil emulsion A at a water cut of 70% exhibited a shear-thinning behavior (right panel in Figure 2). Waxy crude oils B and C and their emulsions showed a strong shear-thinning
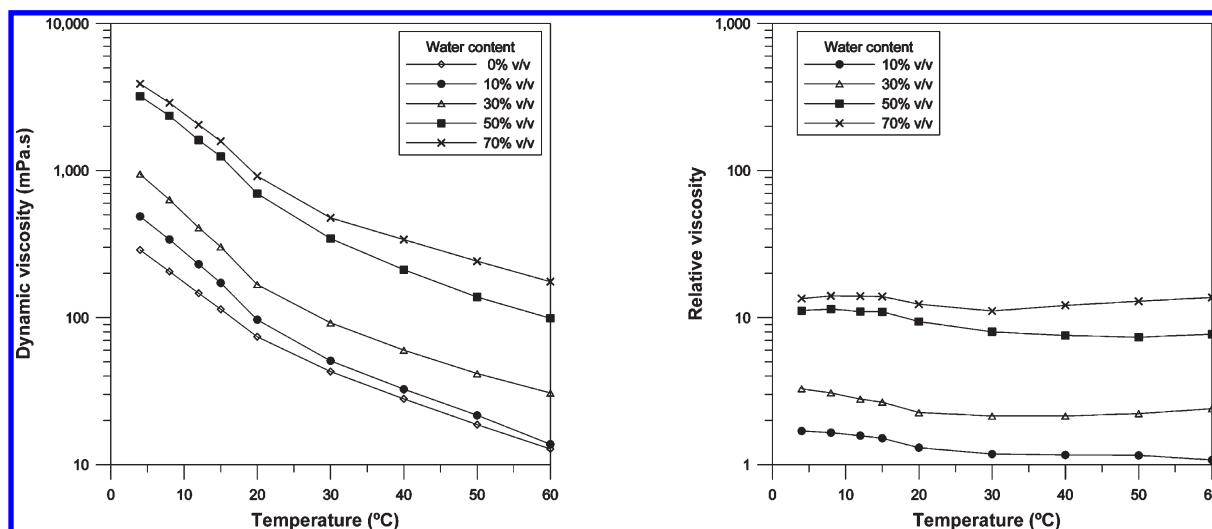
Figure 1. Dynamic viscosity (left) and relative viscosity (right) versus the temperature for waxy crude oil A at a shear rate of 50 s^{-1}.
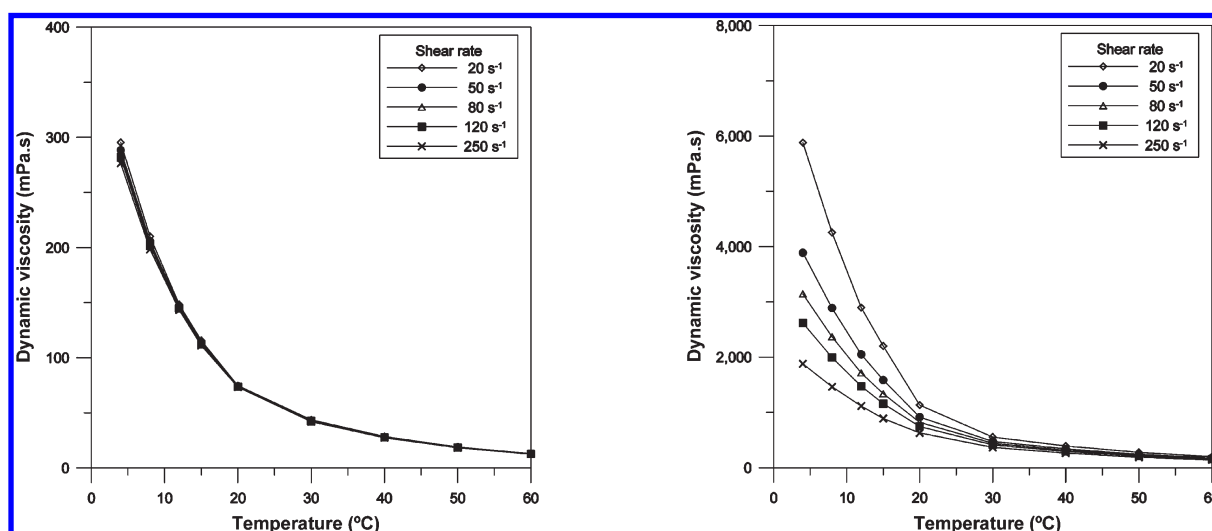

Figure 2. Dynamic viscosity versus the temperature at different shear rates for crude oil A (left) and the emulsion with 70% water content (right).
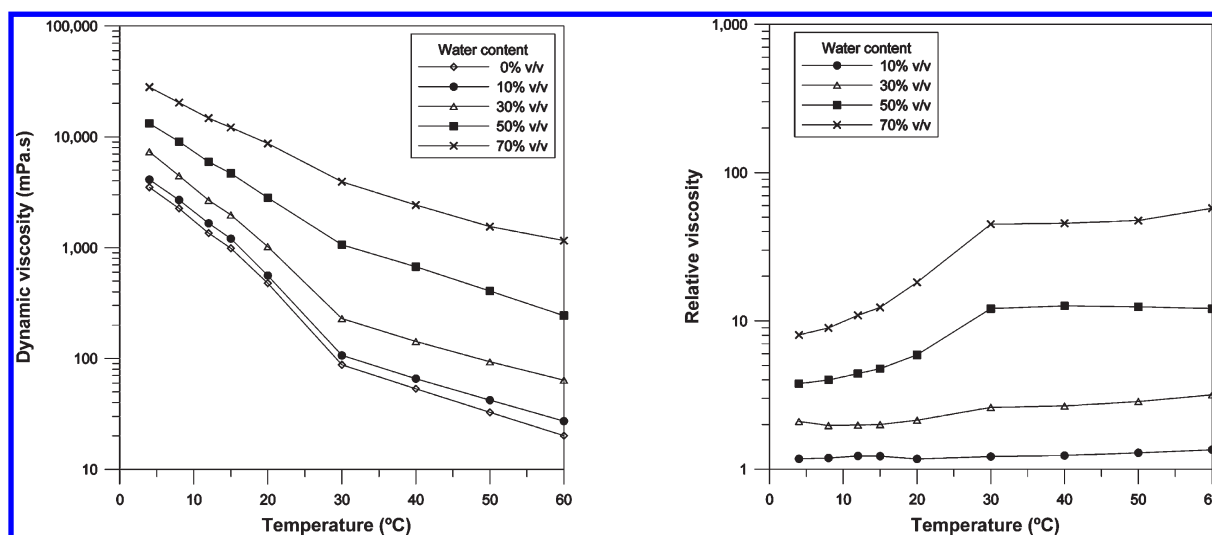

Figure 3. Dynamic viscosity (left) and relative viscosity (right) versus the temperature for waxy crude oil B at a shear rate of 50 s^{-1}.

behavior below WAT (Figure 4 and 6) characterized by Ostwald exponent *n* (Table 1) values ranging from 0.19 to

0.99, respectively. Figures 3 and 5 display the viscosity according to the water cut for waxy crude oil emulsions B
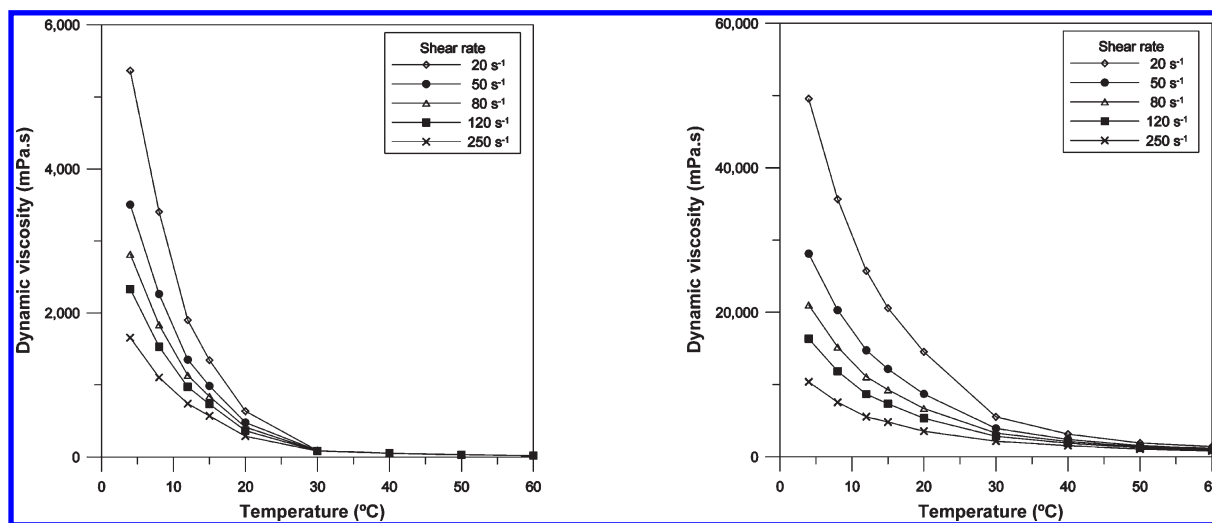
Figure 4. Dynamic viscosity versus the temperature at different shear rates (20, 50, 80, 120, and 250 s^{-1}) for crude oil B (left) and the emulsion with 70% water content (right).

Figure 5. Dynamic viscosity (left) and relative viscosity (right) versus the temperature for waxy crude oil C at a shear rate of 50 s^{-1}.

Figure 6. Dynamic viscosity versus the temperature at different shear rates (20, 50, 80, 120, and 250 s^{-1}) for crude oil C (left) and the emulsion with 70% water content (right).
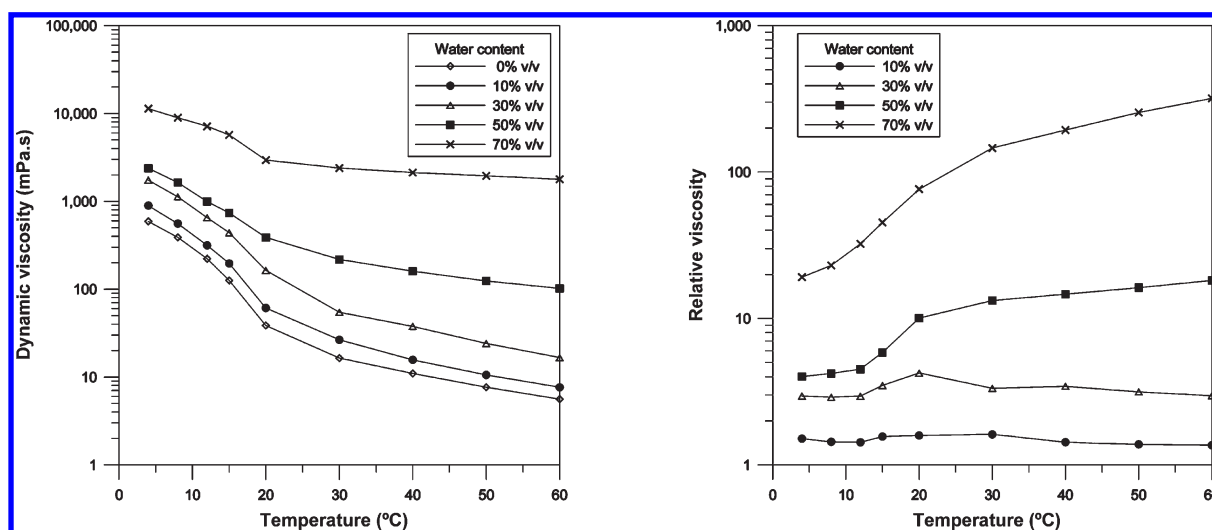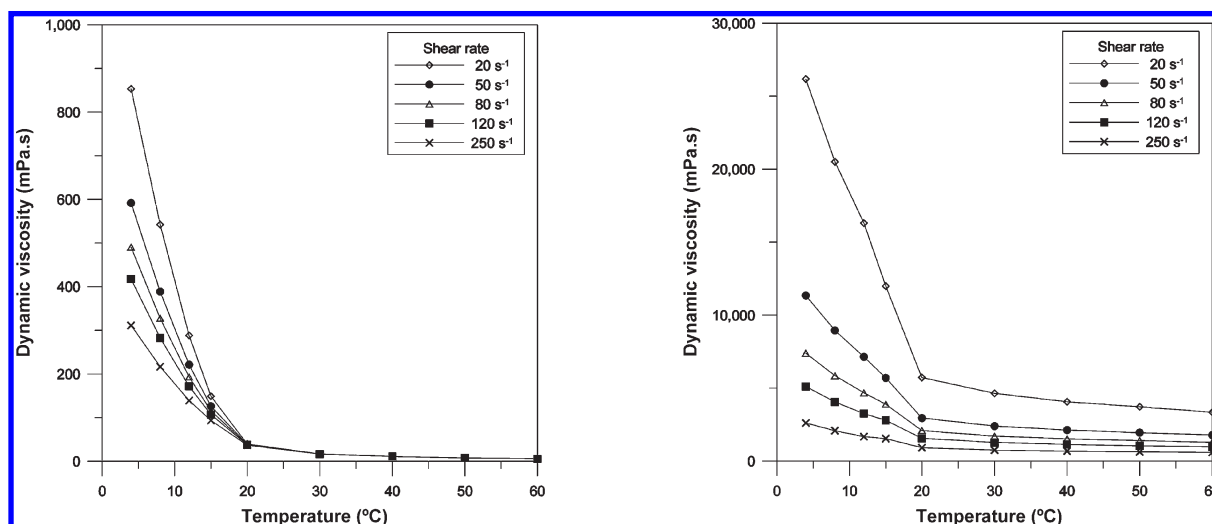
and C, respectively. Below a 50% water content, the viscosity change behaved following a normal pattern for the majority of waxy crude oils, as observed with crude oil A (Figure 1). This is important because the water fraction produced from a well generally increases over time. On the other hand, these crude oil emulsions showed very high viscosity with 70% of the water content, and their appearance was gel-like (Figure 7).

Table 1. Ostwald Parameters Based on Flow Curves of Waxy Crude Oils and Emulsions

			Ostwald parameters	
crude oil	temperature	water cut (%)	K	n
A	40.0	1.0	0.03	0.99
A	15.0	1.0	0.12	0.98
A	40.0	70.0	0.63	0.84
A	15.0	70.0	6.44	0.64
B	40.0	0.7	0.06	0.98
B	15.0	0.7	3.71	0.66
B	40.0	70.0	7.35	0.72
B	15.0	70.0	115.27	0.42
C	40.0	0.8	0.01	0.99
C	15.0	0.8	0.26	0.82
C	40.0	70.0	33.94	0.29
C	15.0	70.0	136.71	0.19

Figure 7. Waxy crude oil B emulsion appearance at 22 °C.

The relative viscosity of the crude oils were calculated by eq 1 and plotted in the right panels of Figures 1, 3, and 5. As can be observed, the relative viscosities are 14, 60, and 320 for crude oils A, B, and C emulsions with 70% of the water content at 60 °C, respectively. The sharp increase of the viscosity for crude oils B and C in comparison to crude oil A indicates the gel structure formation.

The analyses of the particle size distribution show that crude oil emulsion A has a polydispersive distribution size and confirmed the presence of tight emulsions, with an average droplet size of 5.2 and 7.3 μm at 70% water cut for crude oils B and C (Figures 8). The droplet size distribution in an emulsion depends upon the interfacial tension, shear rate, nature of emulsifying agents, presence of solids, and bulk properties of oil and water. For these reasons, the droplet size distribution can define the emulsion stability and should be considered. In general, the smaller the average size of the dispersed water droplets, the more stable and viscous the emulsions.

Crude oils A, B, and C had a WAT event at higher values than room temperature (Table 3), and the emulsions from the crude oil with higher asphaltenes content appeared to be more viscous. These results could indicate a tendency of the interaction between wax (as a solid particle) and asphaltene, although a wide range of the asphaltene concentration should be studied to better understand the possible relation.

In multi-phase production scenarios, a risk-free crude oil may become subject to the particularities of the flow conditions and restart problems. Current standard tests performed in Petrobras do not include a test for the crude oil pour point and gel rheology as a function of the water content. The objective of this study was to show the significance of considering this issue in flow assurance strategies for the production of waxy crude oils.
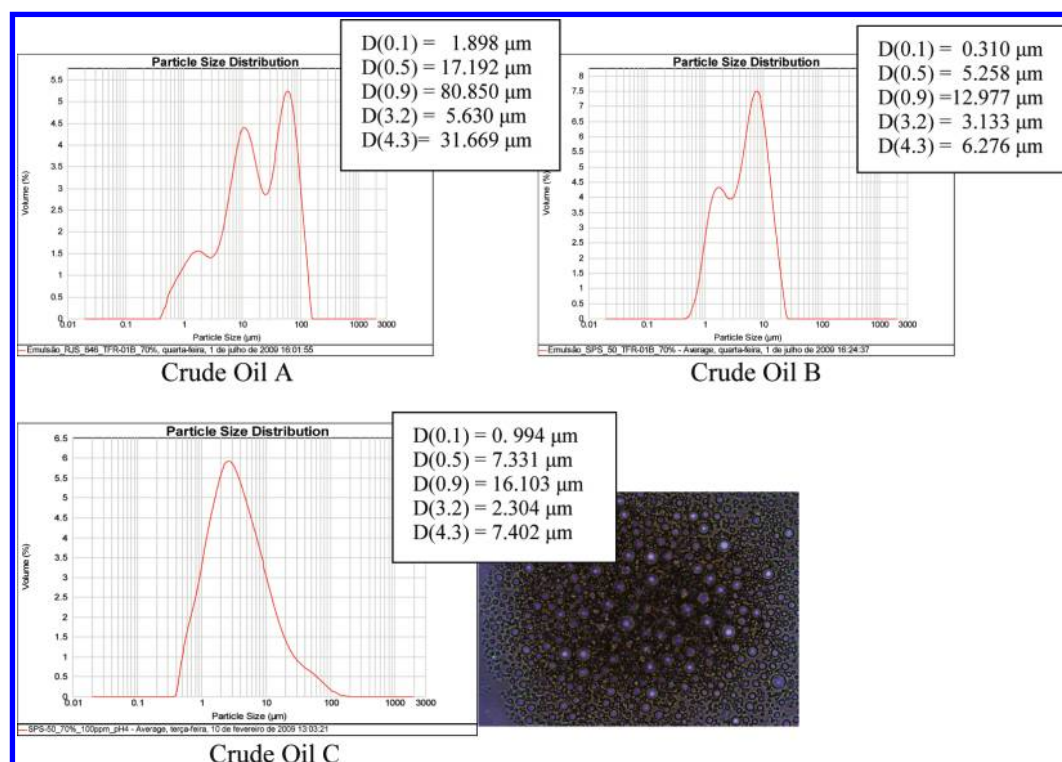

Figure 8. Particle size distribution analysis for waxy crude oils A, B, and C at 70% water cut.

Table 2. Distribution by Carbon Atoms of the *n*-Paraffin Fraction Isolated from the Crude Oils

component	n-paraffins (%)			component	n-paraffins (%)		
	A	B	C		A	B	C
C14		0.01		C39	1.07	0.47	1.05
C15		0.14		C40	0.94	0.48	0.94
C16		0.51		C41	0.93	0.64	0.92
C17	0.03	1.07	0.01	C42	0.83	0.21	0.87
C18	0.1	1.06	0.02	C43	1.29	0.58	0.86
C19	0.3	1.32	0.22	C44	0.80	0.23	0.81
C20	0.63	1.17	1.10	C45	0.85	0.62	0.90
C21	1.29	1.22	2.33	C46	0.85	0.39	0.81
C22	2.19	1.36	3.35	C47	0.80	0.43	0.92
C23	2.87	1.43	3.91	C48	0.90	0.41	0.85
C24	3.32	1.52	4.19	C49	0.78	0.44	0.88
C25	3.48	1.52	4.07	C50	0.86	0.43	0.83
C26	3.91	1.68	4.49	C51	0.88	0.43	0.89
C27	3.93	1.63	4.21	C52	0.92	0.23	0.83
C28	3.84	1.57	4.16	C53	0.85	0.69	0.94
C29	3.52	1.4	3.57	C54	0.91	0.44	0.84
C30	3.02	1.21	3.03	C55	0.92	0.47	0.89
C31	2.62	1.05	2.46	C56	0.81	0.41	0.82
C32	2.18	0.91	2.07	C57	0.92	0.49	0.88
C33	1.98	0.91	1.84	C58	0.91	0.45	0.78
C34	1.71	0.72	1.59	C59	0.81	0.47	0.87
C35	1.55	0.69	1.42	C60	0.58	0.45	0.87
C36	1.41	0.37	1.43	C60+	34.78	64.62	29.00
C37	1.25	0.54	1.20	total	100.00	100.00	100.00
C38	0.68	0.49	1.08				

Table 3. Physical–Chemical Properties of the Studied Waxy Crude Oils

analysis	crude oil		
	A	B	C
API	27.8	26.6	31.1
water (% w/w)	1.0	0.7	0.8
SARA (% w)			
saturates	57.1	51.2	57.2
aromatics	24.5	24.2	26.2
resins	18.0	23.1	14.7
asphaltenes	0.4	1.5	2.0
resin/asphaltene	45.0	15.4	7.4
TAN (mg of KOH/g)	0.27	0.23	0.03
WAT (°C)	35.2	46.1	36.5
n-paraffin content (% w)	5.6	10.6	10.8

To better understand the behavior of these emulsions, chemical analyses were performed and procedures have been established to study crude oil and emulsion characteristics.

We can underline here that the use of rheological means is a good way to understand and assess the gel behavior of waxy crude oil emulsions. The future work will be focused on the study of the yield stress of these waxy crude oil emulsions to estimate the stress below which it does not flow using a smooth stainless cone–plate geometry.

3.2. Chemical Analysis. *3.2.1. Separation and Characterization of the n-Paraffins from These Crude Oils.* The wax content is assumed to represent the total amount of *n*-paraffins in each crude oil. The wax content obtained for crude oils A, B, and C was respectively 5.6, 10.8, and 10.6% (by weight percent).

It was observed that, the higher the content of *n*-paraffins in the oil, the more stable the emulsion formed. Analysis of the fraction rich in paraffins, using HTGC associated with HTSD, showed a higher content of long-chain paraffins (C60+) for all oils when compared to the usual results obtained for other oils analyzed by Petrobras, as can be seen in the distribution by the carbon number for the three oils, which is shown in Table 2.

Heavy *n*-alkanes play an important role in the paraffin crystal formation process. Long-chain paraffins can precipitate when the oil is cooled (below the cloud point or WAT) because of their low solubility in this medium. When a sufficient amount of crystals have precipitated, they overlap each other and form a gel with solid-like properties.[9] It has been observed that only small volumes of *n*-paraffin fractions are needed to form gel, because of the large aspect ratios of the crystals. This phenomena has been observed with as little as 0.5% wax[9] and 3–4%.[8]

It is important to emphasize that the phenomenon of the gel network cited was observed in oils, with temperature reduction, and not in emulsions, as is the case of the present work. There is little information about the formation of

waxy gel emulsions in the literature. The work of Visintin et al., which proposes a qualitative interpretation of the structure of waxy crude oil gels in the presence of water, can be mentioned. In this paper, the authors propose a mechanism in which wax particles are adsorbed at the liquid–liquid interface, forming pickering emulsions, increasing the interfacial film viscosity, and reducing the coalescence of the drops.[11] Then, the growth of the gel network involves the droplets themselves, and the gel behavior emerges when the entire volume is spanned by a wax crystal network. However, the mechanism of formation of these emulsions is not quite explained.

Also, a relation between the increase in the viscosity and *n*-paraffin content was observed but not with C60+ fractions. In sample C, the content of C60+ was practically the same as found in sample A. These observations suggest a more complex phenomena involving the presence of paraffin in these systems. Even with theses observations, it is not well-understood how the wax particles interact at the interface and asphaltenes seem more likely to be the components responsible for the interaction between the droplets and wax molecules. Considering a low bulk concentration of 1.5–2.0%, it may be enough to represent a relatively high concentration at the interface.

An increase in the asphaltene content and a decrease in the resin/asphaltene relation (Table 3) as functions of viscosity enhancement to samples A, B, and C were observed. These results were also determined by Paso et al.,[10] who reported that the stability of the Brazilian waxy emulsions was a consequence of the greater abundance of asphaltenes and the reduced abundance of resins.

3.2.2. Emulsion Studies. Most emulsion studies take into consideration crude oil properties (polar components presents in oil) because it is not possible to analyze directly the components in the water–oil interface. In some cases, a centrifugation procedure can be applied to generate an interface between the oil and water phases.[14−16] Then, the interface can be analyzed and studied to understand the behavior of polar components in a water–oil interface. In studied emulsion samples, this procedure was not successful when trying to obtain a rag layer by centrifugation because of the high viscosity samples.

A different approach to compare each sample emulsion was made based on phase separation by centrifugation and further solvent extraction. A centrifugation procedure

(14) Varadaraj, R.; Brons, C. *Energy Fuels* **2007**, *21*, 1617–1621.
(15) Gu, G.; Zhang, L.; Wu, X. A.; Xu, Z.; Masliyah, J. H. *Energy Fuels* **2006**, *20*, 673–681.
(16) Xu, X. A. *Energy Fuels* **2008**, *22*, 2346–2352.

Table 4. Results Obtained in Fractionation of Emulsion Samples

soluble fractions	emulsion samples		
	A	B	C
hexane (%)	22.7	19.6	15.2
toluene (%)	1.1	0.9	0.8
relation hexane/toluene	20.6	21.8	19.0
insoluble residue (mostly salt, water-soluble species) (%)	14.3	6.4	13.9
evaporation losses (%)	61.9	73.1	70.1

was made in the emulsions to concentrate the interface material. As a result, separated oil (resolved) and emulsion (nonresolved) phases were obtained. This "new emulsion" (nonresolved) with the interface material theoretically concentrated was dried, and a solvent extraction was applied to separate fractions as a function of polarity (using hexane and toluene as solvents).

When the results obtained are analyzed (Table 4), similar results to all three samples can be observed, with a slight decrease of toluene-soluble fractions with an increase in the viscosity. Also, there was no significant difference between the hexane/toluene-soluble relationships. The results (spectrum) from analysis of infrared spectroscopy of toluene soluble in all three fraction samples indicated a rich aromatic fraction as expected (asphaltene compounds are concentrated in this fraction). This indicates the presence of these compounds as emulsion stabilizers at the interface. The observation of an aromatic fraction in the emulsion (toluene soluble) could be related to the results observed in SARA analysis and asphaltene content in the crude oil.

In crude oil characteristics, there is a clear relationship between resin/asphaltene and viscosity behavior. This was not observed in the emulsion fractionation results. The toluene-soluble yield and the relationship between hexane/toluene results were similar to all three samples. Considering these two different approaches, there are two important points that should be discussed. First of all, the ratio between emulsion viscosity and resin/asphaltene occurs when crude oil properties are considered. However, it cannot be confirmed whether or not the distribution of the asphaltenes (and resins) in emulsion follow the same trend. The second point is the definition of resins and asphaltenes. These definitions are based in class solubility, and plenty of compounds are present in toluene-soluble fraction. Considering these definitions and the Soxhlet procedure approach studied here, some relationship between emulsion fractionation results and emulsion stability would be expected, as observed in crude oil properties; however, this relationship was not observed. With these results, it was not entirely possible to conclude that the resin/asphaltene relationship and asphaltene content are responsible for the emulsion stability increase observed.

The contribution of the resin/asphaltene relationship in emulsion stability has been reported in other studies. Czarnecki's work[17] questioned the participation of asphaltene molecules in the stability mechanism. In a more recent report, the same author mentioned that the composition of material found at the surface of water droplets is different from the composition of asphaltenes, resins, and the parent oil.[18] Additionally, studies of waxy gel formation in the presence of different asphaltene polarity fractions reported a greater gelation temperature reduction when a less polar asphaltene fraction is present because of the similarity at the molecular level.[8] In other work, the importance of the aliphatic nature of asphaltene in waxy gel characteristics is mentioned.[9] Consideration of just these properties (resin/asphaltene and asphaltene content) could result in a misconception of emulsion stability models in waxy gel systems. However, the presence of these polar components in the oil–water interface is clear.

4. Conclusion

The association of paraffinic solids in crude oil generates an extended network structure, especially when the volume of dispersed water is above 50%. Above this value, there is a sharp increase in the shear viscosity.

Waxy crude oil with low viscosity can produce very stable and viscous emulsions that increase gel strength and hinder pipeline restart. In this work, we have shown that the presence of water increases the magnitude of the rheological properties of waxy crude oil gel. This characteristic is attributed to the network developed by the aggregation of the waxy crystals and water.

The superior viscosity in waxy emulsions B and C is a consequence of the greater abundance of *n*-paraffin. High-temperature chromatography analysis of the fraction rich in paraffin showed a higher content of long-chain paraffin (above C60+) for all three crude oils. A comparison of polar component results obtained in crude oil and emulsion analyses suggest a more complex interaction in the interface. Considering only the asphaltene content or asphaltene/resin relationship could result in a misconception of emulsion rheology models in waxy gel systems.

With the increase of multi-phase production in offshore environments, which are characterized generally by low ambient temperatures, it becomes important to evaluate the pressure drop near the gel point of the crude oil emulsions.

These results suggest that the impact of waxy crude oil gel emulsion needs to be considered in the standard tests conducted on crude oils during field development studies, particularly for those offshore developments with multi-phase production.

In future studies, the analysis of the internal structure of the gel and its droplet size distribution could be made. Analyses of the *n*-paraffins obtained from the oils, such as the average molecular weight of those heavy fractions and separation of polar components present in the interface, can also be performed.

(17) Czarnecki, J.; Moran, K. *Energy Fuels* **2005**, *19*, 2074–2079.

(18) Czarnecki, J. *Energy Fuels* **2009**, *23*, 1253–1257.
(19) Hénaut, I.; Brucy, F; Vincké, O. SPE 56771, 1999.