



Particles formed by interfacial material and paraffin wax on the formation and stabilization of water-in-oil emulsions with low contents of asphaltenes

Lina R. Morantes¹, Oscar J. Martinez-Villabona¹, Vitoria R. Gomes¹, Marcia C. K. de Oliveira², Ana M. Percebom^{1*}

¹ Department of Chemistry, Pontifical Catholic University of Rio de Janeiro (PUC-Rio), Brazil

² PETROBRAS Research, Development and Innovation Center (CENPES)

*apercebom@puc-rio.br

Abstract

Asphaltene are known to be the main responsible for crude oil emulsion due to their activity at the water-oil interface. However, even oils with low asphaltene contents produce stable emulsions, suggesting the contribution of other oil fractions capable of forming colloidal particles. This study investigates the role of interfacial materials and paraffin waxes extracted from Brazilian crude oils in water-in-oil emulsions. Besides chemical composition, the colloidal structures formed by these fractions were characterized using polarized optical microscopy and small-angle X-ray scattering (SAXS). The study also investigated the behavior and physicochemical properties of emulsions formed by the fractions in a model oil and emulsions formed by crude oil after removing interfacial material or paraffin wax. The correlation among the results indicated that interfacial materials form nanostructures which are important for emulsion formation due to their amphiphilicity but are not sufficient for emulsion stabilization. Surprisingly, their removal improved emulsion stability due to increased viscosity, suggesting they act alongside other oil fractions. On the other hand, paraffin waxes cannot promote emulsion formation without an amphiphilic component. Still, they are essential for emulsion stabilization even at temperatures higher than the temperature of their crystallization in the crude oils (WAT – wax appearance temperature). Besides, the stabilization mechanism is unexpectedly not by the lamellar network but by Pickering particles of wax crystals. The findings highlight the importance of polar oil fractions, other than asphaltene and paraffin waxes, in governing emulsification, enhancing understanding of waxy crude oil emulsion.

Keywords

Pickering Emulsion; Scattering; Pre-salt

Introduction

Numerous studies have highlighted the pivotal role of asphaltene, followed by resins, in forming interfacial films that stabilize petroleum emulsions [1-4]. However, despite their low asphaltene content (<3%), certain Brazilian crude oils still face emulsification challenges. For these oils, it raises the question of whether interfacial materials solely facilitate emulsion formation by reducing surface tension or if they contribute to other stabilization mechanisms, such as forming a steric barrier.

To address this, separating the interfacial materials (IMs) from crude oils enables studying them in model emulsions and residual oils post-material removal. One hypothesis suggests that IMs' self-assembly could lead to colloidal aggregates formation, potentially serving as Pickering stabilizers.

Furthermore, despite their low asphaltene content, certain Brazilian crude oils exhibit stable emulsions and are rich in paraffin waxes. This observation prompts the hypothesis that paraffin wax crystals, acting as solid particles, might contribute to emulsion stabilization. However, the exact role of paraffin waxes in stabilizing crude oil emulsions remains incompletely understood.

To elucidate these mechanisms, scattering techniques for colloidal characterization of these aggregates emerge as crucial tools. This study sheds light on the potential role of IMs and paraffinic crystals in stabilizing crude oil emulsions. Therefore, we conducted a comprehensive physicochemical characterization of interfacial materials [5] and paraffin waxes [6] in low asphaltene crude oils. Additionally, we studied IMs and paraffin waxes in model solvents and

emulsions and analyzed emulsions formed by residual oils post-fraction removal [5-6].

Methodology

PETROBRAS Research, Development, and Innovation Center (CENPES) provided three medium-density crude oils from Brazilian fields, and their physicochemical properties are described in Table 1.

Table 1. Physicochemical properties of crude oils provided by CENPES.

	O1	O2	O3
Saturates (wt %)	45.5	58.1	66.1
Waxes (wt %)	-	5.96	5.01
Aromatics (wt %)	32.8	24.7	19.1
Resins (wt %)	19.2	17.1	14.4
Asphaltenes (wt %)	2.4	<0.5	<0.5
API (°)	21.4	28.9	30.7

The samples were named with the following abbreviations: O for crude oils, IM for interfacial material, and W for waxes. FIM was added to the names of residual oils free of the IMs. Moreover, a number is added to the sample's name to inform the oil source. O1 is the only acid crude oil in this study because it has a total acidity greater than 0.5 mg KOH g⁻¹. O2 and O3 are waxy crude oils with 5.96% and 5.01% paraffin wax content, respectively.

The interfacial material extraction was adapted from the method described by Jarvis et al. [7], using 10 times the amount of crude oil and 35 times the amount of hydrated silica to increase the yield of isolated interfacial material.

Paraffin waxes, W2 and W3, were obtained from O2 and O3 by precipitation with acetone according to an adaptation of the Universal Oil Products (UOP) method 46-64 [8]. The residual oils from this first step correspond to the maltenes, named M2 and M3, which are the asphaltenes-free oils. The supernatant from the extraction was roto-evaporated to recover the oils free of paraffin waxes (also free of asphaltenes due to the first step). They were named wax-free oils: WFO2 and WFO3. It is worth mentioning that the wax-free oils are also free of asphaltenes because the removal of wax requires a previous extraction of asphaltenes. W3 was purified using a silica gel column to remove the polar material remaining in the wax after precipitation. The procedure was based on the method described by Musser and Kilpatrick [9], and the purified wax was named W3-P.

Brine and the oily phase were mixed in a 30:70 volume proportion for emulsion preparation. This mixture was heated to 80 °C for 1 h and manually mixed for 60 s for a preliminary homogenization.

The mixture was stirred at 8000 rpm for 3 min to form the emulsions, using an Ultra Turrax T25 rotor-stator homogenizer. They were characterized at the micrometric scale using a Bel Engineering MPL-2 optical microscope with a light polarizer, transmitted illumination, and a 5x/0.12 or 10x/0.25 objective lens.

Ultra-small, small-, and wide-angle X-ray Scattering (USAXS, SAXS, and WAXS) experiments were performed at room temperature on the laboratory-based XENOCSS 1.0 XEUSSTM equipment at the Institute of Physics, University of São Paulo. A GeniXTM source generated CuK α radiation of 8 keV and $\lambda = 1.54 \text{ \AA}$. The sample holders were glass capillaries, or Kapton® windows, set at a distance from the detector of 1.2 and 3.8 m to SAXS and USAXS, respectively. Images were collected with a 2D Dectris 300K (for USAXS and SAXS) or 100K (for WAXS) Pilatus detector. The resultant intensity curves, $I(q)$, as a function of the scattering vector, $q = 4\pi\sin\theta/\lambda$, being θ the scattering angle and λ the wavelength, were analyzed with SASFit software version 0.94.11 and fitted with the Beaucage model for complex systems with multiple size-scale structures in a unified Guinier-Power law approach [10].

Results and Discussion

Adding interfacial materials to a brine and mineral oil mixture under stirring formed W/O emulsions. From visual inspection, the formed emulsions were opaque brown, had a viscosity similar to mineral oil, and coalesced in less than 10 minutes, except for the emulsion formed with IM2, which coalesced after around 30 minutes. This observation indicates that IMs have a fundamental role in emulsion formation but not in emulsion stabilization, or at least not without other components.

The SAXS curves obtained for IMs in the model solvent were fitted to the Beaucage model [10], which indicates that they are formed by hierarchical particles. This model can provide the power-law exponents (P) and Guinier radius (Rg) with two organization levels, where level 1 corresponds to small-scale sub-particles, and level 2 represents clusters formed by the assembly of the sub-particles. P values give information about the fractality of the objects and can be correlated to values previously reported in the literature to obtain information about their shape and surface. The samples of IMs in model solvent presented Rg1 varying from 26 to 125 Å and a considerable difference in the values of P1. The sub-particles of IM1 were in the threshold between a mass and a surface fractal (P1 = 3), but the sub-particles of IM2 and IM3 (P1 ~ 1) must be mass fractals of low-dimensional objects, for example, randomly distributed rods or chains.

Similar to the fractions, the curves from crude and residual oils also exhibited two different decays, indicating a hierarchical structure. According to SAXS results, the extraction of IMs strongly

modified the aggregation behavior in oils, forming larger sub-particles and smaller and more fractal clusters and inducing self-organization. These results can help understand the colloidal properties of the crude oils and the roles of IMs to correlate with their effects on the emulsification properties. WAXS curves of O2 and O3 presented weak signals at $q = 2.18$ and 2.47 \AA^{-1} , whereas O1 and NA1 presented no signals at this q -range. They coincided with the peaks observed for resins from the same crude oils. Interestingly, the signals became stronger after removing interfacial materials, and an extra peak at $q = 1.76 \text{ \AA}^{-1}$ appeared for O3FIM, which was also observed for resins.

Resins usually solvate asphaltenes in crude oils rather than forming ordered aggregates [32]. However, O2 and O3 have a higher proportion of resins to asphaltenes than O1, which may be the reason for the self-organization process of the resins in these crude oils. Our group is currently investigating this topic.

W/O emulsions were formed with brine and the different oils (O1, O2, O3), including the residual oils obtained after IMs extraction (O1FIM, O2FIM, O3FIM) to elucidate the role of these fractions. The emulsions were light brown, had a higher viscosity than the crude oils, and did not phase separate after one year at room temperature. Optical microscopy allowed the comparison of the droplets' morphology and sizes and the verification of crystalline materials' presence using polarized light. All the emulsions formed spherical droplets, but they had different sizes. Droplets from the emulsion formed with O1 were smaller than those formed with O2, which were smaller than those formed with O3. The emulsions of the waxy crude oils, O2 and O3, presented birefringent particles. After removing IMs, droplets from the emulsions of O1 and O2 decreased in size but did not change for O3. The amount of birefringent material in the emulsions of O2 and O3 significantly increased after IM extraction. We speculate that this extraction favored the crystallization of paraffin wax present in O2 and O3.

The droplet size reduction after IM removal was unexpected because this fraction is often described as a promoter of emulsification. Although the extraction does not necessarily remove IMs completely from the crude oils, the amount removed was enough to form emulsions with significantly smaller droplets, which may also have important implications for stability.

The reduction of droplet size and the higher stability after removing IMs can be due to the increased viscosity. Besides, the structural changes observed by SAXS, including the induced self-organization, can be the reason for the increased viscosity.

SAXS analyses of paraffin waxes reveal intriguing features that shed light on their crystalline structures. At $23 \text{ }^\circ\text{C}$, no Bragg peaks are observed (Fig. 1). However, SAXS analyses of the fraction of

saturates obtained from the same parent crude oils in another study indicate the presence of a peak at 0.14 \AA^{-1} , corresponding to 45 \AA . These results suggest that components of the saturates other than waxes play a role in their self-organization. However, they do not explain the birefringence observed in polarized micrographs of the paraffin waxes. The WAXS curves of W2 and W3 exhibit peaks corresponding to the arrangement of paraffinic chains, which is the cause of the birefringence. The peaks are identified by the Miller indices (hkl) of their corresponding crystalline planes, allowing the identification of an orthorhombic structure [28]. These peaks for an orthorhombic crystal system were attributed to the hkl reflections as (110), (020), (120), (210), (220) to W2 and (110), (020), (120), (210), (130), (220) to W3 and W3-P.

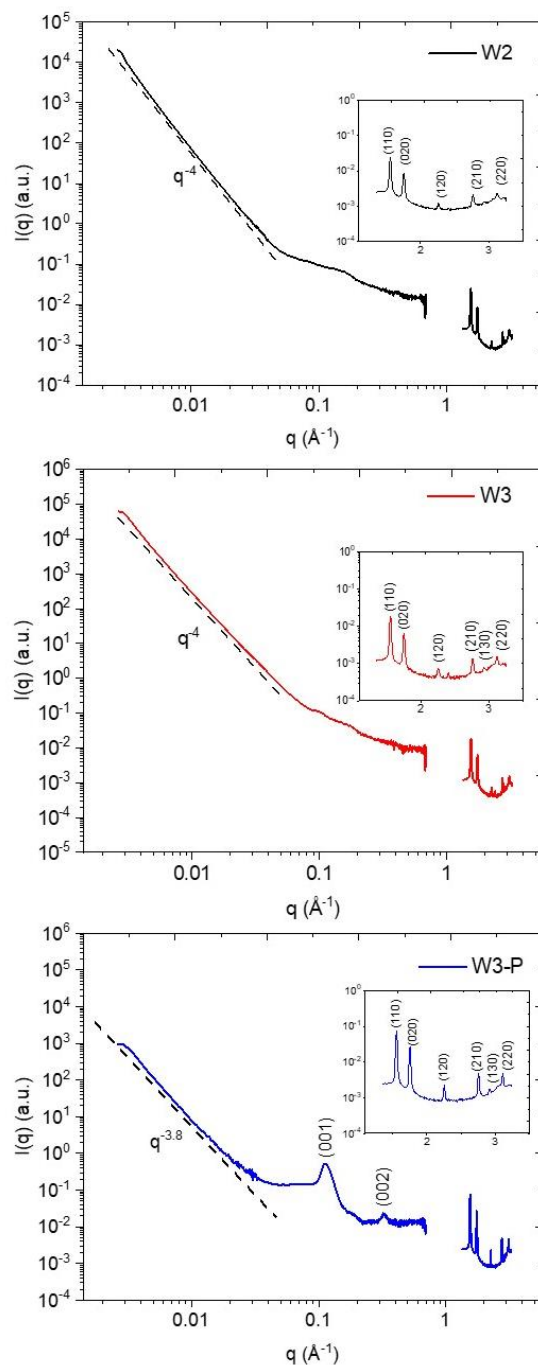


Fig. 1. USAXS/SAXS/WAXS curves obtained at 23 °C for the extracted paraffin waxes, W2 and W3, and for the purified wax, W3-P, with their fractal scale (q^D) and lattice spacings (hkl) of crystalline planes for orthorhombic structures.

The peaks in WAXS region provide cell parameters of $a = 4.7 \text{ \AA}$ and $b = 7.2 \text{ \AA}$ for W2 and W3, corresponding to the distance between paraffinic chains forming crystalline particles in two-dimension axes ($c = 0$). Although the peaks observed for waxes are not observed for their parent crude oils O2 and O3, these peaks are present in the WAXS curves of emulsions prepared with these oils (at $q = 1.56 \text{ \AA}^{-1}$ and 1.75 \AA^{-1}). It indicates that waxes concentrate at the water-oil interface, favoring self-organization in emulsions more than in the oil bulk. The self-organization of crystalline paraffin wax particles at the interface may be responsible for the stabilization mechanism.

W3 exhibits a peak at $q = 2.41 \text{ \AA}^{-1}$, absent in W3-P. An ongoing project indicates that resins from the same oil exhibit a peak at the same position. After purification, W3-P exhibits peaks in the small-angle region (Fig. 1C) with the relative position corresponding to a lamellar structure, where the peaks at 0.11 and 0.22 \AA^{-1} were attributed to the hkl reflections as (001) and (002). The purified wax is organized in the three-dimension axes ($c \neq 0$).

The value of q of the first peak indicates the interlayer distance ($d = 2\pi/q = 57 \text{ \AA}$) and allows the calculation of the mean carbon atom number chain ($n_c = 43$). Organizing the paraffin waxes into a lamellar phase requires a high level of purification, so it is unexpected in the crude oil bulk and emulsions. Indeed, the peaks corresponding to the lamellar phase were not observed in the SAXS region of crude oils and emulsions prepared with them.

In the present study, the orthorhombic arrangement of paraffinic chains indicates the formation of crystalline particles, presenting birefringence in polarized micrographs of W2, W3, and their parent crude oils. However, the absence of peaks corresponding to lamellar liquid crystalline phase in W2, W3, crude oils, and emulsions of these crude oils means that waxes do not form a lamellar network at the nanoscale when they are not highly purified. The need for highly purified paraffin wax to create a lamellar phase suggests a Pickering stabilization of W/O emulsions.

Although the differences in the physicochemical properties of the waxes are subtle, O2 and O3 form emulsions with different characteristics. Observing emulsions over time and at various temperatures highlights these differences. We compared emulsions of crude oils and oils without specific fractions (asphaltenes and waxes) to identify their effects on the properties of emulsions. Therefore, the oily phase used in the emulsification was crude oil (O2 or O3), an oil without asphaltene, i.e., the maltene (M2 or M3), or an oil without asphaltene

and wax (WFO2 or WFO3). The method of wax extraction requires the previous removal of asphaltenes, hindering the obtaining of crude oil with asphaltene and without wax.

All emulsions are brown to black and visually more viscous than crude oil. However, they differ in stability, as shown by the stability tests at 25 and 60 °C and in optical microscopy images (Fig. 2 and 3).

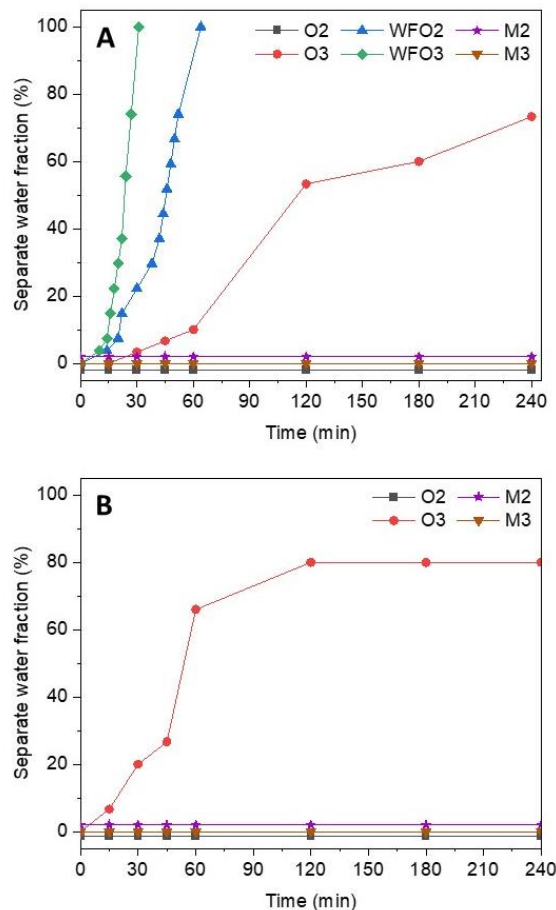


Fig. 2. Fraction of water separated from different emulsions over time in stability tests (A) at 25 °C and (B) at 60 °C. The emulsions were prepared with brine and different oily phases: crude oils, O2 and O3, wax-free oils, WFO2 and WFO3, and maltenes, M2 and M3.

Emulsions were prepared with brine and different oily phases: crude oils, O2 and O3, wax-free oils, WFO2 and WFO3, and maltenes, M2 and M3. During the stability tests, the O2 emulsion remains stable for at least 4 h at 25 °C, while the aqueous phase begins to separate from the O3 emulsion after 30 min. The fraction and speed of separation are increased in the tests at 60 °C, separating approximately 80 % of the total water from the O3 emulsion. However, O2 is stable even at 60 °C. Temperature significantly affects paraffinic oil emulsions, but O2 emulsion is remarkably stable compared to O3 emulsion.

The droplet size is highly related to the emulsion's kinetic stability. Optical micrographs show that the water droplets are larger for O3 ($17 \pm 15 \mu\text{m}$) than for O2 emulsion ($7 \pm 6 \mu\text{m}$), consistent with

observed stability behavior, considering the coalescence related to larger droplet size. Birefringence is observed in both emulsions, indicating the presence of crystalline particles. Microscopy does not reveal if they were at the interface or dispersed in the oily phase. The emulsions prepared with crude oils O2 and O3 present peaks corresponding to the waxes in the WAXS curves, whereas O2 and O3 do not present any diffraction peak at 23 °C. Hence, forming a water-oil interface favors the self-organization of crystalline paraffin wax particles in emulsions more than in the oily phase.

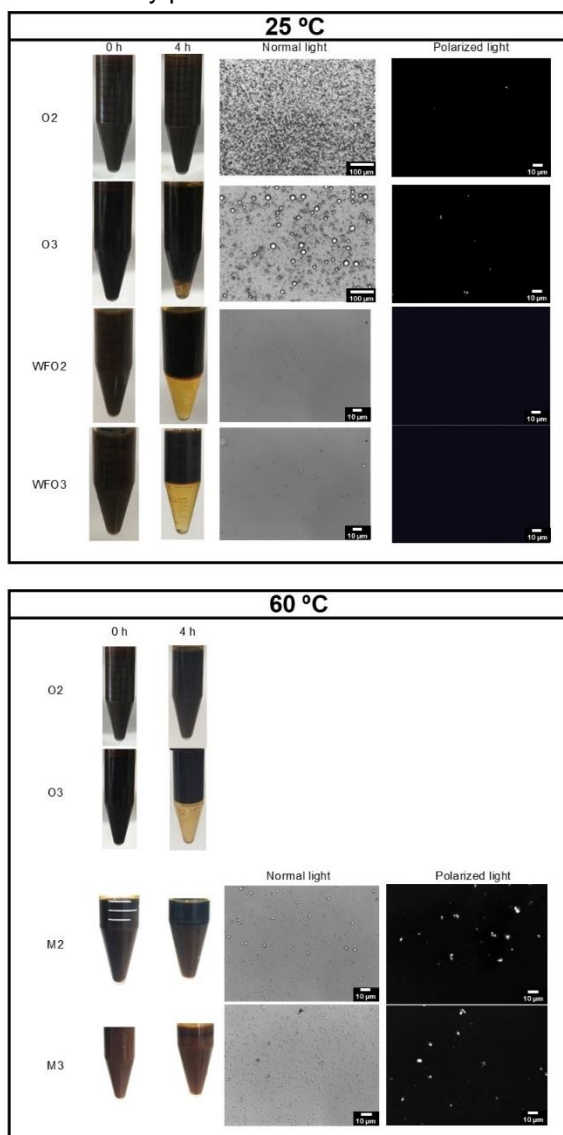


Fig. 3. Photographs of stability tests of different emulsions and optical micrographs in bright field and polarized light at 25 and 60 °C.

Emulsions prepared with wax-free oils are unstable, with total coalescence in less than 30 and 60 min for WFO3 and WFO2, respectively. However, wax-free oils are also free of asphaltenes, indicating that at least one of these fractions is essential to stabilization. The higher stability of WFO2 emulsion could be related to the higher content of resins in O2 than in O3 (Table 1). This hypothesis is under investigation in another

study of our group. Microscopy images of WFO2 and WFO3 emulsions show a low fraction of droplets with dimensions of $0.3 \pm 0.2 \mu\text{m}$. However, the small droplet size is probably because the large droplets had already coalesced due to the lack of stability in the absence of paraffin wax and asphaltenes. Furthermore, there are no birefringent materials in micrographs of WFO2 and WFO3 emulsions, indicating that waxes or asphaltenes are responsible for the previously observed organized structures.

The removal of waxes is not possible without prior removal of asphaltenes. Hence, to isolate the effect of wax in the emulsions, maltenes (M2 and M3, which are asphaltene-free oils) were also used to prepare emulsions for comparison with results from wax-free oils, WFO2 and WFO3. The stability test of the M2 emulsion at 60 °C shows the separation of the oil phase (Fig. 3), known as oiling off. This effect is only observed in the absence of asphaltenes, indicating their importance for the miscibility of the oil components. However, the aqueous phase did not separate even upon heating for emulsions prepared with maltenes M2 and M3 (Fig. 3). Therefore, the extraction of asphaltenes from waxy oils does not induce the coalescence of water droplets and even increases emulsion stability when comparing M3 with O3 emulsions (Fig. 3). We speculate that asphaltenes removal could allow more interactions between paraffin waxes and other petroleum fractions, such as resins or aromatics, which could be the reason for the increased stability.

Asphaltenes removal also reduces droplet size in emulsions of M2 ($0.3 \pm 0.1 \mu\text{m}$) and M3 ($0.5 \pm 0.4 \mu\text{m}$), favoring kinetic stability, with coefficients of variation reduced to 0.33 and 0.8, respectively. Although the droplet sizes of wax-free oils (WFO) emulsions and asphaltene-free oils (M) have the same order of magnitude, they have different stability behaviors. M emulsions also present birefringence in optical microscopy with more and larger crystals ($\sim 5 \mu\text{m}$) than crude oil emulsions ($\sim 1 \mu\text{m}$). The peaks in WAXS results are more intense for M3 emulsion than for O3 emulsion and absent in WFO3 emulsion, confirming the increase in crystallinity after asphaltene removal. The formation of more crystals in M emulsions, which are the most stable ones, corroborates our hypothesis of stabilization by crystalline particles of paraffin wax.

In summary, M3 emulsion has the same droplet size as WFO3 emulsion. However, the former has more birefringent material and is much more stable, indicating that droplet size is not the main parameter for the stabilization. The presence of paraffin crystals increases with asphaltene removal and is essential to avoid coalescence. This fact is intriguing because the temperature of 60 °C is much higher than the wax disappearance temperature (WDT) from both crude oils (40.7 and 32 °C). However, the melting of isolated W2 and W3 (87 and 83.5 °C) is still higher than the WDT of

the crude oils, and maybe a small amount of crystalline wax particles might remain at 60 °C and stabilize the emulsions. This observation confirms the hypothesis that the emulsions are not stabilized by a lamellar network but possibly by small Pickering particles of paraffin wax. We assume O2 emulsion must be more stable because it has a higher WDT than O3. This effect may be related to the higher amount of waxes or aromaticity of O2 than O3 (**Table 1**). Given their role as Pickering stabilizers, even slight changes in particle structure could impact the emulsification process.

Conclusions

The comprehensive investigation into the role of interfacial materials (IMs), particularly their amphiphilic nature, in emulsion formation and stabilization underscores their fundamental significance. Visual inspection of W/O emulsions formed with IMs revealed their crucial role in initiating emulsification processes. However, they do not have a relevant role in stability, as shown by the rapid coalescence of model emulsions. SAXS analysis further elucidated the hierarchical structure of IMs, shedding light on their aggregation behavior and the influence of extraction on oil properties. Notably, removing IMs led to structural modifications in oils, influencing emulsion stability and droplet size distribution.

The presence of paraffin waxes emerged as a key factor in emulsion stabilization, particularly through a Pickering mechanism. WAXS analysis provided insights into paraffin waxes' crystalline structures, revealing their self-organization propensity at the water-oil interface. Emulsions prepared with wax-free oils exhibited reduced stability, highlighting the indispensable role of waxes and asphaltenes in stabilization.

Removing asphaltenes surprisingly enhanced emulsion stability, suggesting complex interactions between different petroleum fractions.

Optical microscopy and stability tests underscored the intricate relationship between emulsion properties and the composition of crude oils.

The presence of waxes influenced droplet size, birefringence, and stability, with implications for emulsion stability at varying temperatures. Furthermore, the observation of increased crystallinity in emulsions post-asphaltene removal supports the hypothesis of stabilization by crystalline paraffin wax particles.

In summary, this study highlights the multifaceted nature of emulsion stabilization, with interfacial materials and paraffin waxes playing pivotal roles in forming and stabilizing emulsions. Further research into the interplay between different petroleum fractions and emulsion properties promises to advance our understanding of emulsion behavior and optimization strategies for diverse applications.

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Responsibility Notice

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