



Usefulness of Interfacial Rheology for Crude Oil Production

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Abstract

The formation of water-in-oil emulsions in crude oil production can lead to a dramatic increase in viscosity, being a crucial matter for flow assurance. These emulsions are stabilized by the indigenous asphaltenes, resins, and naphthenic acids, while chemical demulsifiers can be used to break them. In this work, we present three different techniques that can be used to assess the properties of asphaltenes, maltenes, and demulsifiers at interfacial level. Shear interfacial rheology tests showed that asphaltene films are more elastic than the maltenes ones. However, when a demulsifier is added, the interface elasticity decreases. Dilatational interfacial rheology investigated the elasticity of the maltenes fraction, which is not well evaluated by the shear interfacial rheology. It was found that maltenes can form elastic interfaces over time. Another technique employed was the Langmuir trough, that allows assessment of the phase transitions in the π -A isotherms. Asphaltenes formed more organized films, while films of the maltenes and of the demulsifier showed less organized structures. The demulsifier was also able to reduce the asphaltenes' initial organization. The calculated compressional elastic modulus confirms the demulsifier effect, namely, less organized structures imply less rigid films.

Keywords

interfacial rheology; emulsions; viscoelasticity

Introduction

The production of crude oils often occurs with the co-production of large amounts of water. In many cases, this water is entrapped in the oil in the form of water-in-oil (w/o) emulsions, which can drastically increase the viscosity of the produced fluid, leading to a major flow assurance problem.

Crude oil emulsions are stabilized by indigenous surfactants, such as asphaltenes, resins, and naphthenic acids. Asphaltenes lead to the formation of rigid interfacial films, and, consequently, to very stable emulsions [1-7]. Resins and naphthenic acids, present in the maltenes fraction, can also promote emulsion stabilization, and present a synergistic effect with asphaltenes [7-11].

Different techniques can be used to break w/o emulsions, one of the most common being the use of chemical demulsifiers. These chemicals interact with the natural surfactants' pre-existing interfacial films, usually disrupting them and hence improving the occurrence of coalescence [12-13].

Therefore, the mechanical (or rheological) behavior of the interfacial films is of great interest in emulsion stability studies, since it ultimately controls the emulsion breakage process. To assess the interfacial mechanical behavior of the films formed by all these amphiphiles, shear and dilatational interfacial rheology can be very useful.

In this work, these three techniques were employed to investigate the interfacial properties of an asphaltene and a maltene fraction, as well as an ethylene oxide/propylene oxide (EO/PO) chemical demulsifiers.

Methodology

Materials

Deionized water (DW) and synthetic brine (SB) were used as the aqueous phase. SB was composed by 77.78 g/L of NaCl, 7.33 g/L of CaCl₂, 2.73 g/L of MgCl₂, 0.75 g/L of KCl, 0.48 g/L of SrCl₂, and 0.39 g/L of Na₂SO₄. All salts were analytic grade, purchased from Sigma-Aldrich, and used without further purification. Liquid vaseline (Vas) (Synth) was used as the oil top phase for interfacial phase transitions tests. Asphaltenes and maltenes (which present resins and naphthenic acids) fractions were obtained by n-heptane (Quemis) precipitation of a heavy oil. Pluronic L-35 (Sigma-Aldrich) was used as EO/PO demulsifier. Chloroform (Quemis) was used for the preparation of asphaltenes, maltenes, and demulsifier solutions.

Shear Interfacial Rheology

Storage (G') and loss (G'') moduli were obtained in time sweep experiments, using the double wall ring geometry in a Discovery HR-3 rheometer (TA

Instruments). Chloroform solutions of asphaltenes, maltenes, and asphaltenes with EO/PO demulsifier were spread directly into the DW/Air interfaces at 25°C. A strain of 1.0% and a frequency of 1.0 Hz were used.

Dilatational Interfacial Rheology

Interfacial tension (IFT) and dilatational interfacial elastic modulus (E') of the maltenes fraction were obtained using the Tracker-H goniometer (Teclis Scientific), at 70°C. The droplet of the liquid maltene fraction was placed inside the DW bulk phase. The amplitude of oscillation was 6% of the maximum drop volume and the frequency of oscillation was 0.05 Hz.

Interfacial Phase Transitions

The interfacial phase transitions were obtained at 25°C using the Langmuir trough KSV NIMA 1004 (Biolin Scientific). Interfaces of SB/Vas were used, and chloroform solutions of asphaltenes, maltenes, and EO/PO demulsifier were spread directly onto the SB/Vas interface. Compression of 10 mm/min was used. The compressional elastic modulus (K') was calculated from the pressure-area isotherms (π -A isotherms) [14].

Results and Discussion

G' was observed to be larger than G'' for both asphaltenes and maltenes fractions in a DW/Air interface (Fig. 1), indicating a more elastic than viscous interfacial behavior. Also, the asphaltenes fraction provided G' and G'' two orders of magnitude higher than the maltenes fraction, confirming its capacity to form more rigid films than maltenes. When the EO/PO demulsifier was added to the asphaltene film, a reduction of ten times on G' and G'' was observed.

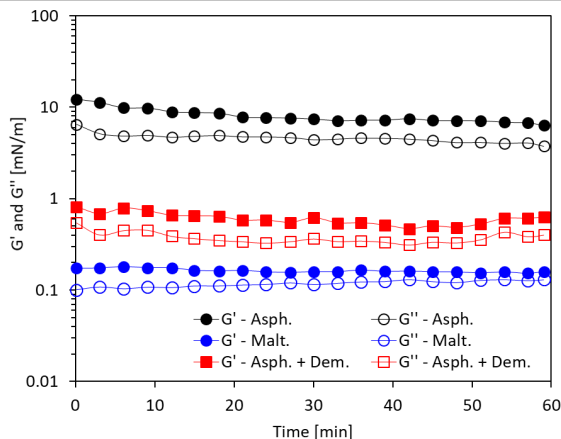


Figure 1. G' and G'' , obtained by shear interfacial rheology, for asphaltenes (black), maltenes (blue), and asphaltenes with EO/PO demulsifier (red), at DW/Air interfaces, 25 °C.

The IFT of the maltenes fraction showed a reduction over the initial 25 min, followed by a constant equilibrium (Fig. 2). This indicates that interface-active molecules in the maltenes fraction, such as resins and naphthenic acids, migrate to the

interface. On the other hand, E' increases almost at the same time interval, indicating that as the amphiphiles migrate to the interface, the film becomes progressively more organized, which results in a more elastic behavior.

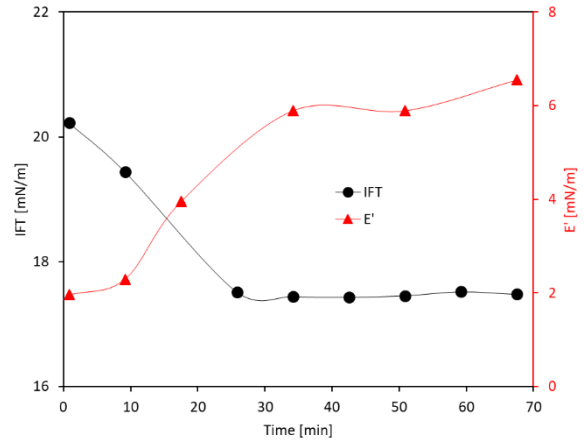


Figure 2. IFT (black) and E' (red) of maltenes fraction and DW, at 70 °C, obtained by Tracker-H goniometer.

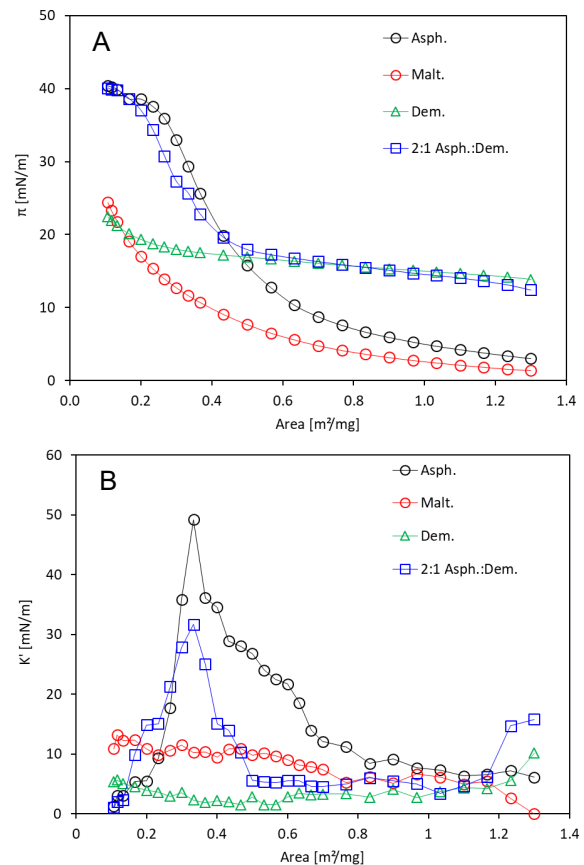


Figure 3. A) π -A isotherms and B) calculated K' for asphaltenes (black), maltenes (red), pure EO/PO demulsifier (green), and the mixture of asphaltenes and the EO/PO demulsifier (blue), at SB/Vas at 70 °C, obtained using the Langmuir trough.

The π -A isotherms of the asphaltenes, maltenes, pure EO/PO demulsifier, and the mixture of 2:1 of asphaltene and demulsifier (Fig. 3A), show different profiles. Initially, the asphaltenes film

presents a liquid expanded phase (LE), followed by a liquid compressed (LC), and then a film collapse, characteristic of a solid phase (S). The maltenes film shows a LE followed by a coexisting phase of LE-LC. This indicates that the asphaltenes film presents a more organized interface, supporting the results obtained with shear interfacial rheology. The EO/PO demulsifier film presents a gaseous phase (G) followed by a LE at very high compressions. When the demulsifier is added to the asphaltene film, changes in the original phase transitions are observed. The film presents a G phase until considerable compression. After that, an LC and S phases are observed. This indicates that, at high compressions, this specific demulsifier leaves the interface and the asphaltenes recover the film organization.

Figure 3 B shows the calculated compressional elastic modulus for each fraction analyzed. In this graph, it is clear the low rigidity of the interfaces composed by maltenes and the EO/PO demulsifier compared to the great rigidity of the asphaltenes film. Another remarkable point is the effect of the demulsifier in reducing the asphaltenes film rigidity. The maximum K' for the asphaltenes film was around 50 mN/m while using the demulsifier, this maximum compressional elastic modulus was reduced to just above 30 mN/m.

Conclusions

Asphaltenes, maltenes (which present resins and naphthenic acids), and demulsifiers were tested by shear and dilatational interfacial rheology, and by interfacial pressure-area isotherms. It was observed that asphaltenes present elastic and rigid films, while maltenes show lower rigidity. The presence of an EO/PO demulsifier disturbs the asphaltenes film organization, leading to softer films. These results, provided by the three techniques, can be useful to assess the interfacial properties of w/o emulsions, as well as to indicate the effect of specific demulsifiers. Therefore, these studies can be used advantageously in flow assurance applications.

Acknowledgments

The authors thanks to Equinor 505 Project P&D ANP n° 20631-8: "Efficiency of Destabilization and Inversion Strategies of Water-in-Oil Emulsions" (PUC Rio/Equinor Brazil Energia/ANP), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, Brazil) for scholarship. This study was financed for Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES, Brazil) – Finance Equinor Brasil.

Responsibility Notice

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