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Influence of the salinity on the interfacial properties of a Brazilian crude oil–brine systems

Douglas R. Alves, Juliana S.A. Carneiro, Iago F. Oliveira, Francisco Façanha Jr., Alexandre F. Santos, Claudio Dariva, Elton Franceschi, Montserrat Fortuny *

Núcleo de Estudos em Sistemas Coloidais/ITP, PEP/Universidade Tiradentes, Av. Murilo Dantas 300, Aracaju, 49032-490 SE, Brazil

HIGHLIGHTS

- We report the effect of aging time at 40 °C on the compressibility of the interface.
- The elastic and viscous moduli increased with the salinity of the aqueous phase.
- The salt leads to a stronger interfacial activity and emulsion stability.

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ABSTRACT

The main focus of the present work was to study the influence of the salinity of aqueous phase on the interfacial properties of a Brazilian crude oil/brine solutions. The pendant drop technique was used to conduct rheological dilatational studies, and a methodology for obtaining important parameters for the rheological study was also presented. The viscoelastic properties were evaluated through dynamic tests that were accomplished up to 24 h. The influence of the interfacial film aging time at 40 °C on the compressibility was also investigated. The results indicated that the values of the total interfacial elasticity and its components, viscous and elastic modulus, were enhanced with the increase of salt content of the brine solutions, suggesting that the salt induces the formation of a more rigid interfacial film. Also the presence of salt led to a stronger interfacial activity of the surfactants yielding higher interfacial elasticity and compressibility.

1. Introduction

In the petroleum industry, the separation of water-in-crude oil emulsions is still a great challenge when one considers high stable emulsions formed along petroleum production pipelines and facilities [1,2]. Besides the decrease in the commercial value of crude oil due to the presence of water, emulsions cause problems in many stages of the petroleum production. Among these problems it can be cited the corrosion in pipes, the deactivation of catalysts and environmental impacts when the produced water is discarded in rivers, lakes and oceans [3–6].

Much attention is devoted to technologies to improve the resolution of these emulsions, and in most cases chemical, thermal and mechanical treatments are combined to provide acceptable efficiencies in the processing. In this scenery, it becomes necessary to identify and know characteristics of the crude oil emulsion in order to better understand the mechanisms involved in the emulsion stabilization and to improve the efficiency of techniques used to promote the phase separation [7]. It is a common sense that one of the main reasons for the stability of water-in-crude oil emulsions is the presence of surface active species commonly found in the crude oil (such as asphaltenes, resins, oil-soluble organic acids, solids and waxes) which may constitute the interfacial film surrounding water droplets. In particular, the formation of a structured film at the interface related to the presence of asphaltene–resin limits the coalescence effect, then the destabilization. These surfactants act modifying the compressibility and rheological properties of the interfacial film [6,8].

The interfacial film formed between the two phases has a resistance to the compression and deformation, producing a barrier that inhibits the droplets coalescence [9–12]. In this sense, the rheological properties of the interfacial film could help to understand the action of a specific surfactant in an emulsion and also the possible mechanisms for the film formation [13]. Also, through the rheological studies of the interfacial film, it is possible to assess the kinetics of the film formation, and information on the adsorption of surfactants and film rupture [4,5].

Using the pendant drop technique, the dilatational elasticity and the compressibility of the film can be obtained through

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* Corresponding author. Tel.: +55 7932182157; fax: +55 7932182190.
E-mail address: fhmontse@yahoo.es (M. Fortuny).

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dynamic tests using the profile of the oil drop (the dispersed phase in this case) inside an aqueous continuous phase [14]. Studies such as those of Yarranton et al. [9] and Yarranton et al. [3] demonstrated a valid correlation between the compressibility, which is related to the rigidness of the interfacial film, with the stability of some crude oil emulsions. In these papers, the increase of the viscoelastic properties, such as elasticity and compressibility, was followed by the enhancement in the time for the interfacial film aging, resulting in a decrease of the droplet coalescence rates. Some studies also indicate that not only the oil phase contributes for the stabilization of crude oil emulsions, but also the characteristics of the water phase, as for example the presence of electrolytes, which may influence the interfacial properties [15,16].

In this sense, the main focus of the present work was to study the influence of the salinity of water phase on the interfacial properties of a Brazilian crude oil/water emulsions. The pendant drop technique was used to conduct rheological dilatational studies, and a methodology for obtaining important parameters for the rheological study was also presented.

2. Materials and methodology

2.1. Materials

Sodium chloride (NaCl), purchased from Merck, and ultrapure water (MiliQ) were used for preparing the solutions. The aqueous saline solutions were prepared at concentrations of 0, 50, and 250 g of NaCl/L with the help of an analytical balance (Shimadzu with a precision of 10^{-4} g). A Brazilian crude oil was sampled in the petroleum field and used in this study. The characteristics of this crude oil (named here Oil 1) are summarized in Table 1. All analyses were performed at Petrobras R&D Centre.

2.2. Viscoelastic properties

In order to assess the influence of the water salinity on the interfacial properties of crude oil/water emulsion, the viscoelastic properties were evaluated through dynamic tests that were accomplished up to 24 h. The influence of the interfacial film aging time at 40 °C on the compressibility of the interfacial film was also investigated.

All dilatational rheology experiments were conducted using a pendant drop tensiometer (Teclis Traker, IT Concept) available at NUESC/ITP in Aracaju/Brazil. In this technique, a sample of oil was inserted in a syringe containing a U needle, which was immersed into the water phase. The interfacial tension measurements were performed by the drop profile, which was digitalized by means of a CCD camera and transferred to a personal computer. The equipment software calculates the dynamic interfacial tension by fitting the drop profile with the Laplace equation coupled with the hydrostatic equation. By using perturbations (typically sinusoidal perturbations [2,10]) of the interfacial area, it was possible to obtain the interfacial elasticity (ε), according to the following equation [1–3,9,10,12,17]:

$$\varepsilon = \frac{d\gamma}{d\ln A} \tag{1}$$

where γ is the interfacial tension response and A is the area of the droplet. The elasticity has a real and an imaginary component, defined by:

$$\varepsilon = \varepsilon' + \varepsilon'' \tag{2}$$

where ε' and ε'' stand for the elastic and viscous modulus, respectively. For the compression tests, after a pre-established aging time, a decrease on the droplet volume is performed, resulting in a decrease in the interfacial area. The compressibility (c) is then obtained by Eq. (3) [3,9].

$$c = \left(\frac{d\ \ln A'}{d\pi}\right) \tag{3}$$

where A' represents the ratio of the resulting interfacial area (end of the compression process) to the initial interfacial area; π stands for the difference between the resulting interfacial tension and the initial interfacial tension.

In this work, the elasticity of the systems was also measured through expansion tests. In these tests, the drop was first expanded and then kept at a constant size while the dynamic interfacial tension was monitored. The maximum interfacial tension right after the expansion was used to determine the interfacial elastic modulus. Drop expansions were performed at triplicates using different and precise values of amplitude in the range between 1% and 6%. The values of elasticity are obtained by the slope of the isotherms which obey the following equation [18]:

$$\varepsilon = \left(\frac{d\pi'}{d\ \ln A/A_0}\right)_T \tag{4}$$

where π is the difference between the final and the initial interfacial tension, A and A_0 stand for the final and initial interfacial area respectively, during the droplet expansion.

The expansion tests have an important characteristic: during the fast expansion there is not enough time for the surfactant adsorption process to occur at the interface. Thus, the dynamic response of the interfacial film is purely elastic, as there is no reorganization processes on the surface [18].

3. Experimental procedure

In the rheological dilatational tests, it is necessary to select adequate values of some parameters in order to evaluate the interfacial properties. Among these parameters, it can be cited the droplet volume, the oscillation amplitude and frequency, and the aging time [10]. For the selection of the optimum droplet volume, the interfacial tension is measured continuously along the time. Typically after 1 h, the curve of interfacial tension becomes nearly constant with time and then a value of the interfacial tension for a specific volume is recorded. The study of the oscillation amplitude is performed by analyzing the constant region of the elasticity in function of time for oscillations of different fractions of the interfacial area. Results for the selection of the droplet volume and oscillation amplitude are presented in the Results section.

The oscillation frequency influences the elasticity values, as for low frequencies the surfactants have sufficient time for diffusion from the fresh interface to the bulk phase. For high frequencies, the diffusion is less important and the instantaneous elasticity is calculated [9]. In this work, it was selected the oscillation frequency of 0.1 Hz, as at this value the self-reorganization effects

Table 1
Characteristics of the Brazilian petroleum used in the work (Oil 1).

Property	Value	Methodology
Density (°API)	28.4	ASTM D-5002
Viscosity at 40 °C	24.6 cP	ASTM D-7042
Water and sediments	0.8% v/v	ASTM D-4007
TAN	0.36 mg KOH/g	ASTM D-0664
SARA analysis Saturated	52.6 wt%	
Aromatics	27.2 wt%	
Resins	19.9 wt%	
Asphaltenes	0.33 wt%	ASTM D-6560