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Interfacial rheology of asphaltene emulsions in the presence of nanoemulsions based on a polyoxide surfactant and asphaltene dispersant

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ABSTRACT

The development of oil-in-water nanoemulsions for application as demulsifiers has attracted a great deal of interest from chemical supply companies in the oil sector, due to the cost savings and advantages of replacing organic solvents with water. In this study, the efficiency of the nanoemulsions developed in a previous work in breaking down water/oil emulsions was correlated with assessments obtained by interfacial rheology studies of the systems used in the preparation of model emulsions. The results show that the performance of nanoemulsions developed for breaking oil emulsions depends on the oil phase used in the system's composition and droplet size distribution. The results obtained from the interfacial rheology confirmed the activity of dodecylbenzene sulfonic acid (LBS) in dispersing asphaltenes in the demulsification step, resulting in more fragile and less elastic interfacial films.

1. Introduction

The stability of water-in-oil emulsions results from the formation of an elastic interfacial film. Soluble aggregates contained in the oil phase are adsorbed at the water-oil interface and form a physical barrier to flocculation and coalescence of the dispersed droplets. The aggregates obtained from the interactions between the asphaltene molecules are known to be the main special species responsible for the stabilization of these emulsions [24,11].

The emulsions stabilized by an interfacial film formed by surfactants (such as resins and asphaltenes) behave as dispersions, where the droplets are formed by a highly resistant viscoelastic film. Therefore, the action of the interfacial film or mechanical barrier formed at the aqueous phase/oil phase interface can be quantified. It has been observed that the stability of an emulsion is closely related to the rheological properties of the interfacial film and that the stability is greater when this film is highly elastic [12,27].

The interfacial rheology describes the functional interplay of the deformation of an interface, the forces exerted on it and the resulting flows in the adjacent phases of the fluid. This can be determined by applying dilation and shear forces [15].

The dilatational interfacial rheology provides a measure of resistance to changes in the interfacial area and can be expressed in terms of the elastic dilatational modulus $|\varepsilon_d|$ (storage modulus) and viscous dilatational modulus $|\eta_d|$ (loss modulus). In interfacial shear rheology, the interfacial area is kept constant and the information about the elastic or storage modulus (G') and the viscous or loss modulus (G'') depends on the frequency applied [24,18,15].

The mechanical properties of asphaltene films at the interface and the influence of the demulsifier on this film can be studied by these methods, which provide valuable information about the origins of the stability of emulsions and the influence of concentration and solvation of resins and aromatic solvents on the adsorption of asphaltenes [24,23].

According to Gafonova and Yarranton [10], the characteristics of the interfacial film formed by asphaltenes depend on their concentration. In systems with high concentration, the asphaltene molecules' configuration changes, allowing them to pack more tightly at the interface, leading to greater coverage of the surface. Larger asphaltene molecules are adsorbed preferentially. Because at low concentration, larger molecules are too scarce to saturate the interface, the smaller ones spread over the interface in the form of a more disorganized plane.

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The effect of aromatic solvents on the adsorption of asphaltenes on water-oil interfaces has been studied and better understood by interfacial rheology. The behavior of asphaltenes in organic solvents is a complex phenomenon related to the solubility of the asphaltenes in these solvents, together with the aggregation behavior. For example, if considering the structural properties of asphaltenes in a solvent composed of toluene and heptane, the asphaltenes precipitate if the solvent has a very high heptane content. Therefore, aggregates of asphaltenes increase in size with higher heptane concentration until the start of their precipitation [14,6].

The effect of the major fraction of an aromatic solvent on the properties of the interfacial film was also observed by Yarranton et al. [28], who explained that the increase of the heptane fraction raises the elasticity of the interfacial film. On the other hand, with a greater fraction of aromatics, the majority of the asphaltene molecules remain in the oil phase instead of moving to the interface.

In earlier studies [25,7], oil-in-water (O/W) nanoemulsions were developed as a new alternative to break down oil emulsions. These nanoemulsions were tested through gravitational separation of oil and water and high efficiencies were achieved, reaching up to 95% depending on the composition of the water/surfactant/oil system present in the nanoemulsion. Some variables presented significant influence on the efficiency and speed of breaking the oil emulsions, such as type of polymeric surfactant used, the polymer employed (where hydrophobicity is a very important parameter) and the type and concentration of the oil phase in the nanoemulsions.

In another investigation, Oliveira et al. [20] developed O/W nanoemulsions with a nonionic surfactant based on ethoxylated castor oil and incorporated it in these systems as an asphaltene dispersant, for the purpose of observing if the presence of this compound promotes more efficient breakdown of the water/crude oil emulsions. The O/W nanoemulsions obtained in that study were efficient in gravitational separation of water from oil, showing excellent potential as demulsifiers in the petroleum industry. However, this efficiency depended on the oil phase and concentration of additive utilized to prepare the nanoemulsions.

The aim of this study is to analyze the rheological properties of the interfacial films of water-in-oil model asphaltene emulsions and to investigate the influence of oil-in-water (O/W) nanoemulsions, with or without a dispersant additive. These water-in-oil model emulsions were prepared with asphaltenes in the heptol (heptane/toluene mixture) solutions and salt water. The results obtained are correlated with the behavior of the interfacial film, composed of asphaltene molecules from the crude oil studied.

2. Experimental part

2.1. Materials

The O/W nanoemulsions analyzed in this study were produced in an earlier experiment and reported in Oliveira et al. [20], using an Avistin EmulsiFlex C5 high-pressure homogenizer (Ontario, Canada). The composition of the dispersions used to prepare the nanoemulsions and their droplet size range are shown in Table 1.

The oil-in-water (O/W) nanoemulsions were composed of:

- Aqueous phase: commercial nonionic surfactant Ultramona®R400 (donated by Oxiteno, Brazil), called in this paper R400.
- Oil phase: (a) xylene, acquired form Vetec Química Fina; and (b) Solbrax Eco, which is a solvent produced and sold exclusively by Petrobras Distribuidora, Brazil. Solbrax Eco 175/225 is mainly composed of aliphatic and naphthenic hydrocarbons, with a distillation range between 175 and 225 °C, and it was characterized in another work [5]. These solvents were used at a concentration of 5 wt% to prepare the O/W emulsions.

In this oil phase, we used dodecylbenzene sulfonic acid (LBS), since in the literature [1,13], LBS is known as a good asphaltenes dispersant. This additive was dissolved in the oil phase (xylene and Solbrax) generating concentrations of 0.05, 0.25 and 0.5 wt%.

The asphaltenes utilized in this study were extracted from a crude oil sample supplied by the Petrobras Research Center (CENPES), Rio de Janeiro, Brasil. The characteristics of this oil were: water content of 0.05 wt%; density of 21.2; saturates content of 40.7 wt%; aromatics content of 34.1 wt%; resins content of 22.9 wt% and asphaltenes content of 2.4 wt% [2].

The solvents *n*-heptane and toluene were used to prepare the asphaltene model solutions. All the solvents were supplied by the company Vetec, Rio de Janeiro, Brazil and were used as received.

2.2. Methods

2.2.1. Extraction of asphaltenes

About 30 g of the petroleum sample was placed under the action of the precipitating agent of the paraffinic solvent (*n*-heptane) in the proportion of 1 L to 30 g for one week under agitation. Then the mixture was filtered twice through filter paper at room temperature (25 °C). The precipitate was passed through a Soxhlet extractor to separate and dissolve the impurities (mainly resins) adsorbed on the asphaltene molecules. The asphaltenes that remained precipitated in the cartridge were extracted with the use of an aromatic solvent (500 mL of dry toluene).

Finally, the solubilized asphaltenes were recovered by evaporating the toluene in a rotary evaporator and then, they were left at rest at room temperature for evaporation of the residual solvent.

2.2.2. Preparation of the model asphaltene emulsions

To assess the influence of the nanoemulsions on model emulsions containing only asphaltenes dispersed in mixtures of solvents as the oil phase, we prepared asphaltenes dispersions in a mixture of two solvents, *n*-heptane and toluene (heptol), in different proportions, which will be detailed later.

Initially, we prepared a dispersion containing 0.50 wt/v% of asphaltenes dissolved in toluene and then diluted it to obtain a dispersion of 0.25 wt/v% of asphaltenes in the proportions of *n*-heptane and toluene (v/v) of 10/90, 15/85, 20/80, 25/75, 30/70 and 35/65.

The water-in-oil model emulsions were prepared at concentrations of 50 v% of oil (asphaltenes in the heptol solution) and 50 v% of salt water, which in turn contained 55,000 ppm of salts (NaCl:$CaCl_2$ ratio of 10:1). The shear force to disperse the oil phase was supplied by a Polytron PT 3100D homogenizer at an agitation speed of 8000 rpm for 3 min, at room temperature. The emulsion preparation method is described in detail by Mansur et al. [17].

2.2.3. Evaluation of the efficiency of the O/W nanoemulsions in demulsifying the model asphaltene emulsions

The efficiency of the gravitational separation between water and oil (in the model asphaltene emulsions) in the presence of the nanoemulsions was measured by the bottle test at 25 °C, also as described by Mansur et al. [17].

The efficiency of each formulation used in the tests was calculated by applying Eq. (1):

$$EF_{WO} = (V_{WS}/V_{TW}) \times 100 \tag{1}$$

where