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Emulsion effects on the yield stress of gelled waxy crude oils

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ABSTRACT

Waxy crude oils subjected to low temperature conditions in ultra-deep water environment for a long enough time start a crystallization process and exhibit a transition to a gel state. Flow assurance is greatly affected by this process. In most cases, this oil has a significant volume fraction composed of water. Hence, it is not uncommon that stable water-in-oil (w/o) emulsions are formed and they co-exist with the paraffinic structure of the waxy oil. The present work analyzes how the volume and dispersion of the droplets in the w/o emulsion influences the rheological properties of the oil when compared with its dry version. In the case of dry oils, the reference for w/o emulsions, we found that the initial temperature of the cooling process affects the yield stress of the material at the final temperature even when T_i is far above the wax appearance temperature. In addition, there is an inversion of the tendency of the growth of the yield stress when T_i is increased. For high values of the cooling rate, we found a second critical stress, besides the yield stress, where a secondary level of structure breaks down. The results concerning the emulsion effects on the yielding behavior of the tested waxy crude oils revealed that small drop emulsions can increase significantly the yield stress. While the typical increase with the volume of water cut was found for large drop emulsions (emulsions with more than 10% of water cut) an even higher level of the yield stress was found for emulsions with less than 5% of water cut. The competition between number of crystal nuclei and size of final crystals have encounter favorable conditions in the case of small drop emulsion. This result is probably related to the fact that the number of initial nucleation points and the distribution of drops in the small-drops emulsions are such that the mean distance between drops are more likely to be covered by the final typical length achieved by the crystals in the cooling process.

1. Introduction

Waxy crude oils make up a significant portion of the petroleum reserves worldwide. Due to the development of new technologies, nowadays it is possible to explore oil basins in deep and ultra-deep water. However, these new areas that are now being explored impose more aggressive environmental conditions, establishing new challenges to flow assurance, a main concern in the oil industry. The low temperatures of this environment, approximately 4 °C, are far lower than the typical Wax Appearance Temperature (WAT), i.e., the temperature where the first waxy crystals are formed in the quiescent fluid. However, more important than that, these temperatures are below the Gelation Temperature (GT), a critical temperature where crystals form a percolated structure and the oil achieves a gel character. Whenever a shutdown occurs, and the oil is exposed to temperatures below the GT for a long period, the gelled character of the oil imposes serious flow assurance problems, since the mobility of this material is greatly diminished: the viscosity increases by orders of magnitude and a visco-plastic character emerges in this process, represented by the appearance of a yield stress. The yield stress, a characteristic strength of the material, is the value that the stress must overcome for a continuous flow to occur. Therefore, it constitutes a crucial parameter that is present in hydraulic plant projects. However, the yielding process of waxy crude oils is very complex and is generally not fully characterized by a single parameter. Because of this fact, this matter has been the main focus of a number of investigations [1–6].

Another important issue to be considered in the flow assurance context is that the oil with emulsions can be found in thermodynamic conditions that are favorable for hydrate formation [7]. Hydrate formation is tremendously harmful for the oil production, since it is common that hydrates promote a complete blockage of the line. This structure is generally accompanied with the appearance of a yield stress

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[8] and are common in the production of oils in a methane-rich environment, but also when there are high levels of CO_2 [9].

An important fact to be considered is that, not rarely, the production of crude oils is accompanied with brine and this mixture is subjected to a turbulent regime generated by valves and other hydraulic accidents. The dispersed water droplets can form a stable water-in-oil (w/o) emulsion especially in the presence of polar compounds such as saturates, aromatics, resins, and asphaltenes (SARA), which are known to play the role of natural surfactants because they carry both hydrophobic and hydrophilic functional groups. Below the WAT, the wax particles exhibit hydrophobic surfaces that can adsorb on the interface of the w/o emulsion by interacting with the natural surfactants already present there. The effect of dispersed water in oil is generally considered in the rheological characterization of the w/o emulsion by generalizing the pioneering work developed by [10]. This path was followed by several publications [11–13] and included non-Newtonian effects. In the case of a quiescent cooling of the emulsified waxy crude oil, it is known that attractive van der Waals forces between the paraffin crystals induce a wax network structure in the droplets' surfaces and the oil phase. It is hypothesized that since the structure of a gelled waxy crude oil includes water drops, these entities act to help the percolation of the network formed by the wax crystals and therefore enhance the mechanical strength of the resulting material subjected to a cooling process. [14] conceived a four stage process for the formation of the structure of the emulsified waxy crude oil below the GT. This process begins with the accumulation of wax particles at the water–oil interface; then there is an increase in viscosity of the interface that increases the stability of the emulsion and decreases the probability of drop coalescence; a third stage occurs when the growth of the waxy structure advances from the water–oil interface and starts linking with other structures; and finally the whole domain contains waxy structures entrapping the droplets of water.

From what was mentioned above, one can conclude that the presence of droplets of water leads to an increase in the pour point temperature as the water cut is increased and such behavior is accompanied by an increase in the corresponding value of the yield stress. Therefore, the problems of production related to emulsified waxy crude oil are seriously worse than for non-emulsified ones. Even with a potentially more harmful scenario, little attention has been paid to the rheological impacts of the cooling process and the gelation of emulsified waxy crude oils. In addition, an analysis of the yielding process of gelled water-in-crude-oil emulsions is an important piece of information which is still lacking in the literature.

Important work conducted in this direction was performed by Visintin et al. [14]. Using a crude oil with high paraffinic content (9.25% wax) and examining water cuts from 10% up to 70%, they reported an increase of both the pour point temperature (from ≈28 °C to ≈34 °C), which can be seen as a proxy for the GT, and the yield stress (from ≈ 100 Pa to ≈ 500 Pa), with the level of water cut. Furthermore, this growth is more pronounced for high water concentrations (above 50%). The criterion for the determination of the pour point temperature and the yield stress was taken to be the point where the storage modulus, G', was overcome by the loss modulus, G'', in a small amplitude oscillatory shear test. This same test was used by [14] to capture viscoelastic effects and they showed that the storage modulus is an increasing function of the water cut in the whole range of temperatures considered. The values of G' increase by orders of magnitude (from ≈ 1 Pa to ≈ 1000 Pa) when the temperature is decreased from 50 °C, and at temperatures below the pour point the storage and loss moduli of emulsion gels were found to grow with time in isothermal conditions. After the structure of the emulsion gels reached equilibrium, for the emulsion gels with a water cut above 35%, there was a power law relation between the storage modulus and the volume fraction of water. They attributed these rheological behaviors to the strong absorption of wax particles at the interface and the resulting entrapment of water droplets, rendering the entire volume eventually spanned by a wax crystal network. The viscosity was shown to be a shear-thinning increasing function of the water cut over the whole range of shear rates analyzed.

Using different samples of waxy crude oils and investigating water concentrations up to 70%, [15] investigated the dynamic and the relative viscosity, i.e., the ratio between the viscosities of the emulsified crude oil and of the dry one. The main results were obtained by expressing the dynamic and relative viscosities as functions of the temperature in two different tests: a) for a fixed value of water cut (70%) and selected shear rates; b) for a fixed shear rate (50 s^{-1}) and selected values of water cuts. The authors showed an increase of viscosity and an increase of the GT for higher water concentrations. Furthermore, the shear-thinning behavior of the viscosity was shown to be more pronounced as the water cut increases.

[16] examined the ice slurries that are formed from water-in-oil-emulsions below the ice temperature (in their case, −10 °C). They analyzed water cuts ranging from 10% to 70% and found no yield stress below 20% for fresh water and 30% for brine. The yield stresses increase from ≈ 300 Pa (water cut below 55%) to more than 3000 Pa (unmeasurable by the rheometric device). [17] also studied ice slurries from water-in-oil-emulsions and found an irreversible breakage process in this kind of material.

The literature that has investigated the rheology of water-in-oil emulsions in the gelled state has not covered a number of important aspects of the yielding process of this kind of material. In this connection, the objectives of the present investigation are to study the effects of the initial cooling temperature, small-drop emulsions (below 5% of water cut), and the cooling rate on the yielding process of waxy crude oil. In addition, we provide some curve fittings of the flow curves obtained for the purpose of capturing the parameters that characterize a broader rheological behavior of the material and not only near the yield stress. The organization of the paper is described next. In Section 2, the experimental procedure is described by presenting the oil employed, the emulsification process together with the drop distribution with respect to the water cut, and the protocol followed in order to take the measurements. Section 3 presents some preliminary results concerning the WAT measurements, the conditions for degradation of the sample, and the effect of the initial temperature effect on dry oil. In Section 4, the main results concerning the effects of the different conditions on the final material are provided. In Section 5, we present some conclusions and a discussion.

2. Experimental procedure

2.1. Oils employed

In the present research, we used oil from two different origins, both of them provided by Petrobras, the Brazilian oil company. Using the method described by [18], we were able to determine the content of asphaltenes and resins of each oil. The first oil, which we will call Oil A, is an oil that was produced from the pre-salt layer at the Espírito Santo basin, off the Brazilian coast. It has a negligible content of asphaltenes and resins. The second one, which we will call Oil B, is an oil that was investigated by [6] and has approximately 3% asphaltenes.

2.2. Emulsification

In the literature there are different methods for preparing water in oil (w/o) emulsions from petroleum [19–21]. We followed the method of [19], which is described in what follows.

(1) Set the oven temperature at 80 °C and wait for 30 min
(2) Measure the masses of the samples of oil and water in different bottles with the corresponding water/oil proportion for every emulsion.
(3) Keep the bottle of oil and the bottle of water inside the oven for one