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RHEOLOGICAL STUDY OF GAS HYDRATE FORMATION; EFFECTS CAUSED BY THE ADDITION OF GAS CONDENSATE TO THE WATER-IN-OIL EMULSIONS.

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Abstract. *Nowadays is known that gas hydrate formation is the biggest problem faced by flow assurance engineers in offshore oil and gas production. Due to the fact that are solid substances that do not flow, they can totally block the pipes causing great economic losses to the oil and gas companies. Several investigations have been made to comprehend and mitigate hydrate formation but this phenomenon still continue to be responsible for the main flow assurance issues and deserves special consideration. In order to better understand the phenomenon of hydrate formation and dissociation the evaluation of the role performed by the different compounds presented in the crude oil can be investigated, since there are crude oils that have more or less tendency to form hydrates. In the presented work, a high pressure cell is used to analyze the rheology of gas hydrate formation from water-in-crude oil emulsions under the effect of gas condensate addition (saturates). The main results obtained are expressed through viscosity curves as a function of the experimental time.*

Keywords: *Gas hydrates, Waxy crude oil, Gas condensate, Pressure cell.*

1. INTRODUCTION

Natural gas hydrates are crystalline water-based solids. They are formed when the water hydrogen bonded (host) encage and hold one or more gas molecules (guests) if typical thermodynamic condictions of high pressure and low temperature are attained (Sloan, 2003). Such conditions are found in offshore oil and gas production. Indeed, in the Brazilian coast most of the gas extractions are favorable to the appearance of hydrate crystal, because the oil reserves are located in ultra-deep water fields (Water deep > 1500) where pressure is high (> 100 bar) and temperature is typically the sea bottom (4 ^{0}C), see Camargo *et al.* (2004) .

Hydrates are solid metastable compounds. There is a pressure-temperature relationship that defines the favorable conditions for hydrate formation or dissociation. After nucleation (appearance of the first hydrates clusters) of hydrates in different parts of the domain, there is a growth of crystalline hydrate structure that is governed by the kinetics of formation of new crystal composition attached to the old (crystallization). Sun and Firoozabadi (2015) indicated that the hydrate surface is hydrophilic and a thin layer of liquid water film is present on the hydrate surface which leads to a capillary bridge between hydrate particles. The strong capillary force holds the particles together, causing its agglomeration. The process of hydrates structures agglomeration occurs in several regions until a critical cluster size is reached. When this happens, an abrupt increment in viscosity is observed until forming a block and plugging the pipeline. As a result of hydrate formation the pressure in the system decreases and at the same time the temperature increases (exotermic process), for more detailed see Webb *et al.* (2012).

To mitigate hydrate blockage several methods have been employeed, as for example, the use of an appropriate subsea layout combined with insulated flexible flowlines, heating, removal free formation water and the most common method is employing chemical inhibitors. The main inhibition methods used in oil and gas industry are: thermodynamic inhibitors (TIs) and low-dosage hydrate inhibitors (LDHIs). TIs such as methanol, glycol and saline solutions act changing the hydrate equilibrium curve. That is to say, the equilibrium temperature of hydrate formation is reduced, shifting the chemical potential of water. Usually, large amount of TIs are required for the process to be effective. In fact, Chen *et al.* (2013) indicated that the quantity of TIs used in a specific case often reaches 20 - 50 wt% or more, which is sometimes not economical. LDHIs are divided in two groups: Kinetic hydrate inhibitors (KHIs) and anti-agglomerants (AAs). LDHIs affect the kinetics of the process, since they delay the crystal growth and avoid the agglomeration, what makes them time dependent. KHIs are polymers of low molecular weight that avoid hydrate formation incrementing the induction time for hydrate nucleation (Chen *et al.*, 2013). Sloan and Koh (2008) reported that when these compounds have a contact with the hydrate surface, they are absorbed by it, and the hydrate formation rate is reduced as well as the crystal grows. KHDIs are usually used in quantities less than 3% of the produced water, reducing the high expenses (Tohidi *et al.*, 2015). Other advantage of KHIs is the synergism that these reagents have with other substances, as monoethylene glycol. On the oter hand, AAs are surfactants soluble in oil that allow the hydrate crystal to form and maintain the hydrate particles in the oil phase avoiding their aggregation. The formed particles are transported by the streamline as a low-viscous liquid and cannot be limited by the subcooling (difference between the system temperature and the equilibrium temperature for hydrate formation).

Surprisingly, despite different preventives and correctives methods, hydrates formation still continue to be reponisble for the main flow assurance issues. Besides that, there is an interesting question in the industry as in the academia: Why are there some crude oils that have more tendency to form hydrates than others, at the same thermodynamic conditions? That concern have been rised when some oil wells have been shuted down, for maintainance for example. Then, there is a limited time to repair and initiallize the operations of the well without the risk of hydrate formation. Probably this limited time is influenced by the chemical compounds of the crude oils. In order to better understand the phenomenon described above, the evaluation of the role performed by the addition of saturates in the crude oil is investigated. The saturates are one of the main constituents of the oil (besides aromatics and polar substituents). The saturate fraction consists of nonpolar material including linear, branched, and cyclic saturated hydrocarbons (paraffins), and when is added to another oil it turns the final blending less viscous.

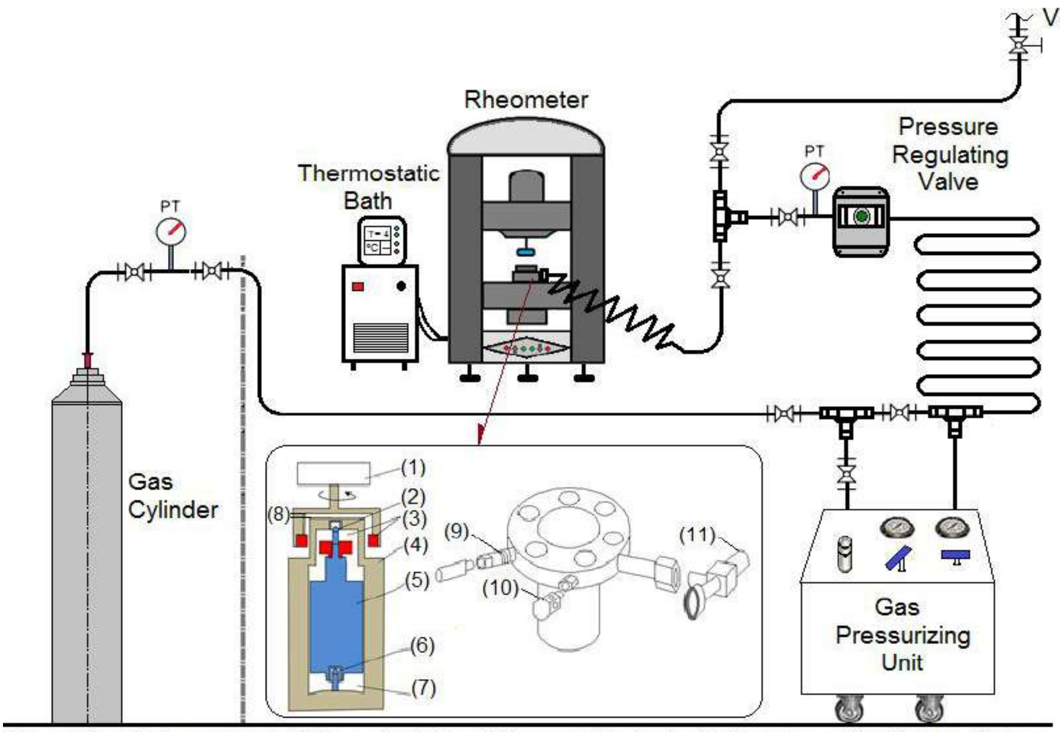
2. EXPERIMENTAL PROCEDURE

A high pressure system is used to conduct the experiments (the same used by Sandoval *et al.* (2018)). The system depicted in Fig. 1 is made up by the gas storage cylinder where pressurized CO2 comes out until a booster, equipment that allows increasing above of 400 bar the initial pressure established in the cylinders. Depending of the experimental pressure studied, sometimes the booster is not required. After that, the pressurized gas is conducted to a serpentine pipe configuration to guarantee a constant rate of gas volume in the pressure cell. The experimental pressure is controlled and set up in a regulating valve before entering to a measured cell. When the experiments have finished, the gas inlet valve of the pressure cell and the regulating valve are closed and the remaining gas in the duct is released through a relief valve.

The measurements are made with a commercial rheometer Haake Mars II (shear-stress-controlled), manufactured by Thermo Scientific, Germany. The rheometer is connected to a thermostatic bath to ensure an accurate temperature control during the experiments. The geometry used is a concentric cylinders PZ35 for pressure cell, as illustrated in the lower rectangle in Fig. 1. The unit consists of two parts. The outer part, which is composed by the cylinder base of the cell (stator) and the magnetic coupling, and by the measuring geometry (rotor), which is supported by two sapphire bearings located at top and bottom within the pressure cell (showing in red color in Fig. 1). A magnetic field created by the two magnets, powers the rotor. The inner magnet is located at the top of the stator, while the external magnet is coupled to the measuring head of the rheometer. All experiments are automatically controlled and the results are extracted with the aid of Haake Rheowin program.

2.1 Procedure

Our crude oil was supplied by the Laboratory of Research and Development of Methodologies for Analysis of Oil (LabPetro). The main characteristics of the oil and gas condensate are shown in Tab. 1. The oil was the same used by Bassane *et al.* (2016). The free formation of water was separated by the gravitational method of the volumetric



Concentric cylinder geometry: (1) Measuring device (2) Upper sapphire beaing (3) Magnetic coupling (4) Stator (5) Rotor (6) Lower sapphire bearing (7) Sample (8) Gap. **Pressure cell**: (9) Pressure sensor (10) Rupture disk (11) Gas inlet.

Figure 1. Sketch of the high pressure rheometer system. Figure taken from Sandoval *et al.* (2018)

flask and the residual water content (emulsioned) was then measured by Karl Fischer titrator technique (ASTM D4377, 2011). Since the oil presented water content in excess of 2% (v/v), it was dehydrated with the add of a demulsifier in a centrifugation equipment. The oil was denominated as "dehydrated oil" when the water content was below of 0.5% (v/v) and was used as a reference for all our experiments. For more details see Bassane *et al.* (2016). The emulsions were prepared rigorously through the following steps: Initially, with the masses of the samples weighted, the oil and deionized water were heated at 60 ^{0}C for 30 minutes in closed bottles. This step is made to improve the oil homogenization and to delete the shear and thermal histories of the oil. After that, the samples were cooled down at the room temperature and mixed manually. Then, the condensate gas was added to the mixture oil-water and subsequently the sample was stirred for 3 minutes at 7500 rpm in a Turrax (model IKA T25) homogenizer to obtain the emulsion (oil-gas condensated-water). A small part of each emulsion was taken to evaluate the drop size distribution. These measurements were conducted in an optical microscope Nikon, model Eclipse LV100POL in the laboratory of characterization and primary process of LabPetro. It was employed the laboratorial instalations and equipment used to measure the drop size distribution by Vargas *et al.* (2018). Representative pictures of the emulsions produced for each gas condensate addition are presented in Fig. 2. Our samples produced stable emulsions with small drop sizes ($3.5 - 5.2\mu m$). The colors of the emulsions were black viscous liquids, classified as entrained water-in-oil type (Fingas, 2014). The forms of the drops were spheric and with homogeneous distribution around the sample and was not observed coalescence between them during three months of monitoring.

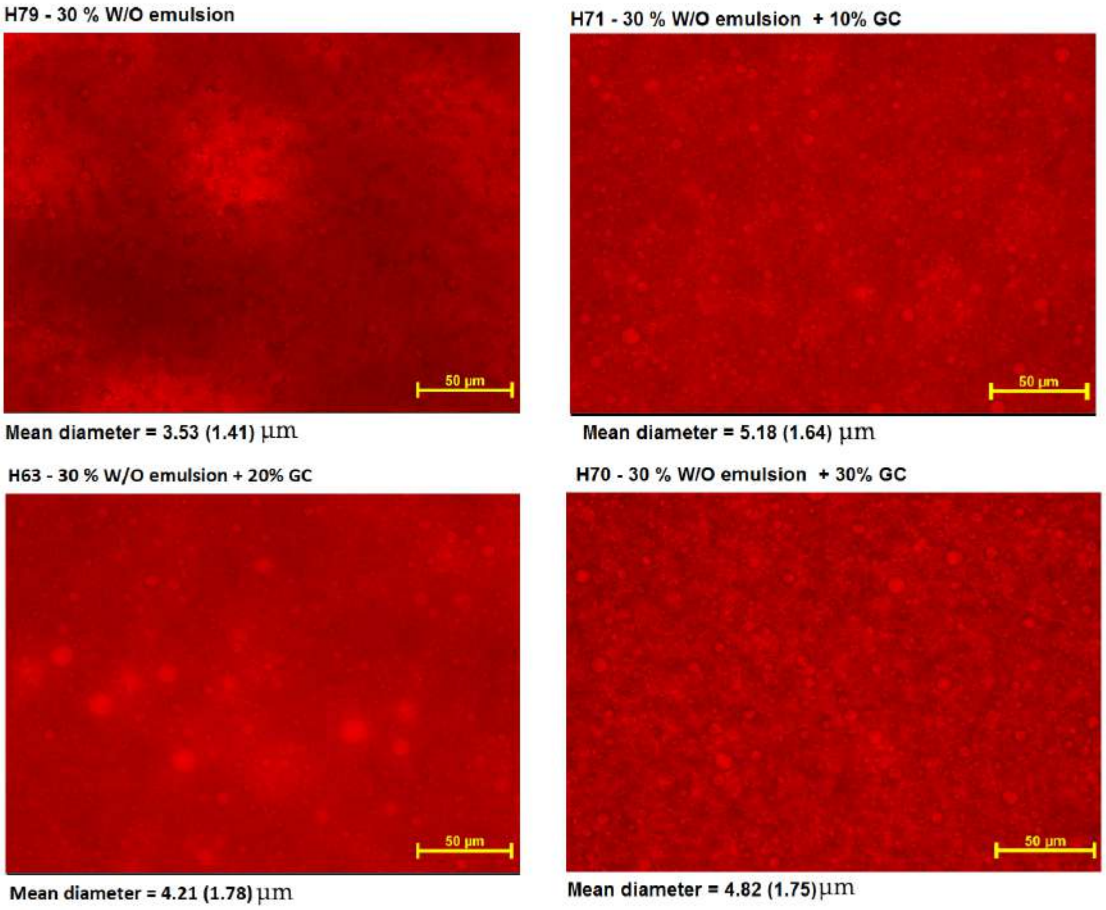
The emulsion was deposited in the cell and pressurized with CO_2 using the high pressure system described above. In an attempt to fully saturate the oil phase with CO_2, the pressure cell was heated up at 80 ^{0}C. This temperature was retained for 8 h, keeping the rotor at constant angular velocity. Next, the sample was cooled until 4 ^{0}C, temperature of hydrate formation. The great majority of the tests were conducted at constant temperature, pressure and rotor angular velocity. These parameters, and other as: influence of water content, salt effect, and a rheological characterization of hydrates were explored by Sandoval *et al.* (2018); Leopércio *et al.* (2016); Webb *et al.* (2014) and Webb *et al.* (2013), among other authors.

3. RESULTS

Before performing the main experimental tests of hydrate formation is necessary to calibrate the pressure cell because there is no mechanical connection between the external magnet and the reometric geometry. Several preliminar tests were conducted to analyze the efectiveness of the pressure cell as: rotor stabilization, friction factor calibration and finally a comparison with other geometries (as plate - plate) in the atmospheric pressure (results not shown). For more details of

Table 1. Properties of the dehydrated oil and condensate gas

Properties	Oil A	Gas condensated	Standard Method
water content (% v/v)	0.420 (0.040)	0.0509 (0.0020)	ASTM (2000)
Density at 20 ^{0}C (g cm^{-3})	0.9310 (0.0030)	0.6734 (0.0050)	ASTM (2009)
Density API at 20 ^{0}C	19.9 (0.5)	76.9 (0.5)	ASTM D1250 and ISO (1996)
Total acid number (mg of KOHg^{-1})	0.400 (0.020)	< 0.010	ASTM (2011)
SARA content			
Saturates (wt%)	41.0 (1.0)	88.70 (0.04)	ASTM D2549
Aromatics (wt%)	31.1 (1.0)	11.10 (0.02)	ASTM D2549
Resins (wt%)	19.0 (1.0)	0.10 (0.01)	ASTM D2549
Asphaltenes (wt%)	8.5 (1.0)	< 0.05	ASTM D6560



H79 - 30 % W/O emulsion
Mean diameter = 3.53 (1.41) µm

H71 - 30 % W/O emulsion + 10% GC
Mean diameter = 5.18 (1.64) µm

H63 - 30 % W/O emulsion + 20% GC
Mean diameter = 4.21 (1.78) µm

H70 - 30 % W/O emulsion + 30% GC
Mean diameter = 4.82 (1.75) µm

Figure 2. Drop size of emulsion with gas condensate and oil A.

these introductory results see the work published by Sandoval *et al.* (2018).
A typical experiment consists in setting up the pressure cell at 60 bar and heat the emulsion (deposited within the cell) at 80 ^{0}C for 8 h. This step permits to dissolve the gas (guest molecule) within the emulsion. After that, the temperature is reduced at a constant rate of 0.6 ^{0}C/min until a final temperature of 4 ^{0}C. This temperature is kept fixed for the rest of the experiment (see the red line plotted in Fig. 3). Then, the termodynamic conditions of hydrate formation are pressure of 60 bar (which is always constant, maintained by the system) and temperature of 4 ^{0}C. These conditions are similar to the ones faced by the oil in real enviroment. For these thermodynamic conditions the CO_2 equilibrium diagram indicates that the subcooling is 6 ^{0}C.

Figure. 3 shows the hydrate slurry viscosity over time for a water-in-oil emulsion with the addition of different gas condensate concentrations. A typical test of hydrate formation is displayed in the orange curve (H70 - 30% GC) of Fig. 3. It is observed an initial viscosity increase after 8 h due to the reduce of temperature until reach 4 ^{0}C. Next, the viscosity

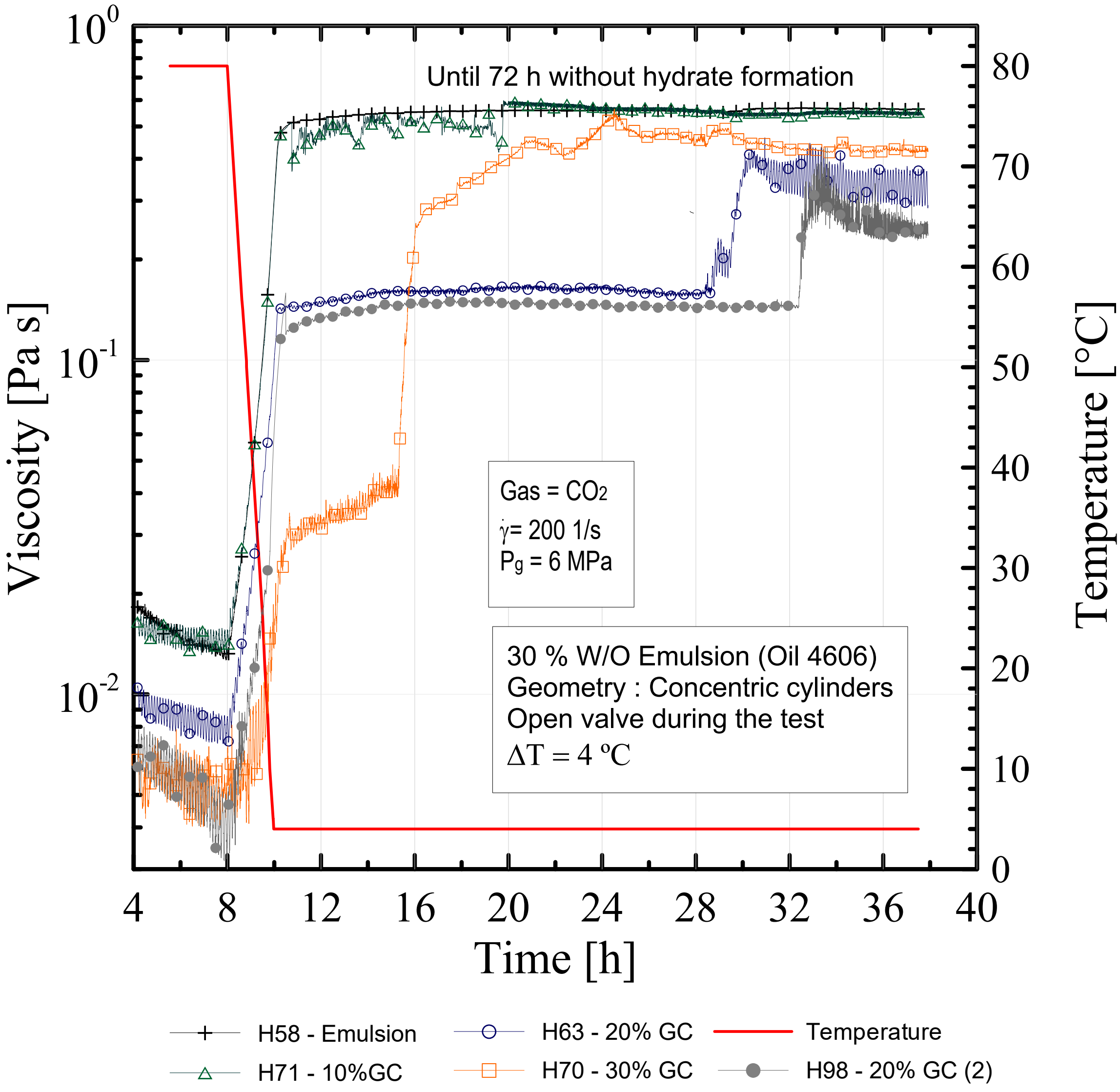


Figure 3. Hydrate formation with addition of gas condensate in oil A.

remains more or less constant for a certain time. This elapsed time is known as induction period, and is characterized by the nucleation and cristallization of hydrates. After that, just after cristallization occurs, a very rapid hydrate growth happens and consequently a viscosity jump is noted due to the cristals agglomeration. Sloan Jr and Koh (2007) reported that during the induction time, hydrate does not form because of its metastable state (unstable at a certain state for a long period of time). The viscosity jump is associated to hydrate formation and it could be observed that the viscosity increased almost 10 times with respect to its previous value. The spike in viscosity is kept for a time, and stars to reduce when the shear forces produced by the rheometric geometry are higher than the cohesion forces of hydrate crystals.

The addition of gas condensate in heavy oils is usually made by the oil industry to reduce the high viscosities, since gas condensate is composed mostly of light components as: pentane, hexane and heptane. Figure 3 depicts one curve with pure emulsion and three with gas condensate addition. The pure emulsion (cross symbol) exhibits a viscosity of 0.55 Pa·s at 4 ^{0}C. Initially, when 10% of condensate gas is added (green triangle) it can be observed that the viscosity does not change at 4 ^{0}C with respect to the original pure emulsion, and was not detected any hydrate formation until 72 h of test. When 20% of condensate gas is aggregated, the viscosity is reduced aproximately 3.5 times and after a 18 h of test (under hydrate formation conditions), hydrate formation is noted. To obtain confidence in our experiments, this test of 20% of condensate addition was repeated in a different day, with another sample (see test H98 of Fig. 3). The difference in the induction time was approximately 4 h. This discrepancy is conservative, since hydrates formation is a stochastic phenomenon. Finally, for the blending of 30% of condensate (orange square) is noticed that the viscosity is diminished around 18 times, but hydrate formation occurs in 6 h, 3 times faster than for the mixture of 20%. Therefore, it can be noticed that the addition of gas condensate reduces considerably the oil viscosity samples, but also increases the risk of hydrate formation.

4. FINAL REMARKS

The behaviour of viscosity hydrate slurries has been analysed in a rheometric geometry as a function of time. The emulsions studied to form the hydrate slurries were previously mixed with gas condensate (natural gasoline). Since gas condensate is usually employed in the oil and gas sector to reduce the viscosity of heavy oils to facilitate its transportation. The main parameter studied in the experiments reported was the induction time, which initiates when the emulsion reaches the termodynamic conditions of hydrate formation (in this case 4 ^{0}C and 60 bar) end ends when a sudden increase in viscosity occurs. As observed in the results, the addition of gas condensate reduces significantly the viscosity of the emulsion at 4 ^{0}C, although it also promotes hydrate formation. As a final comment, this method of mixture deserves special atention in the sense that the suitable quantity of gas condensate added at the thermodynamic condition of hydrate formation should be verified for each oil.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

ASTM, 2000. “Astm D4377 – Standard test method for water in crude oils by Potentiometric Karl Fischer Titration”.

ASTM, 2009. “Astm D5002 – Standard test method for density and relative density of crude oils by digital density analyzer”. *Annual Book of Standards*.

ASTM, 2011. “Astm D664 – Standard test method for acid number of petroleum products by potentiometric titration”.

Bassane, J.F.P., Sad, C.M., Neto, D.M., Santos, F.D., Silva, M., Tozzi, F.C., Filgueiras, P.R., de Castro, E.V., Romão, W., Santos, M.F. *et al.*, 2016. “Study of the effect of temperature and gas condensate addition on the viscosity of heavy oils”. *Journal of Petroleum Science and Engineering*, Vol. 142, pp. 163–169.

Camargo, R., Gonçalves, M., Montesanti, J., Cardoso, C. and Minami, 2004. “A perspective view of flow assurance in deepwater fields in brazil”. In *Offshore Technology Conference*. Offshore Technology Conference.

Chen, J., Sun, C.Y., Peng, B.Z., Liu, B., Si, S., Jia, M.L., Mu, L., Yan, K.L. and Chen, G.J., 2013. “Screening and compounding of gas hydrate anti-agglomerants from commercial additives through morphology observation”. *Energy & Fuels*, Vol. 27, No. 5, pp. 2488–2496.

Fingas, M.F., 2014. “Water-in-oil emulsions: formation and prediction”. *Journal of Petroleum Science Research*, Vol. 3, pp. 38–49.

ISO, 1996. “Iso 12185 – Petroleum products determination of density oscillating U tube method”. *International Organization for Standardization ISO*, Vol. 12185.

Leopércio, B.C., de Souza Mendes, P.R. and Fuller, G.G., 2016. “Growth kinetics and mechanics of hydrate films by interfacial rheology”. *Langmuir*, Vol. 32, No. 17, pp. 4203–4209.

Sandoval, G.A., Soares, E.J., Thompson, R.L., Siqueira, R., de Andrade, R., Campos, F. and Teixeira, A., 2018. “Analysis of co2 hydrates in crude oils from a rheological point of view”. *Energy & Fuels*, Vol. 10, pp. 2733–2741.

Sloan, E.D., 2003. “Fundamental principles and applications of natural gas hydrates”. *Nature*, Vol. 426, No. 6964, pp. 353–363.

Sloan, E.D. and Koh, C., 2008. *Clathrate hydrates of natural gases*. CRC press.

Sloan Jr, E.D. and Koh, C., 2007. *Clathrate hydrates of natural gases*. CRC press.

Sun, M. and Firoozabadi, A., 2015. “Gas hydrate powder formation–ultimate solution in natural gas flow assurance”. *Fuel*, Vol. 146, pp. 1–5.

Tohidi, B., Anderson, R., Mozaffar, H. and Tohidi, F., 2015. “The return of kinetic hydrate inhibitors”. *Energy & Fuels*, Vol. 29, No. 12, pp. 8254–8260.

Vargas, G.G., Soares, E.J., Thompson, R.L., Sandoval, G.A., Andrade, R.M., Campos, F.B. and Teixeirac, A., 2018. “Emulsion effects on the yield stress of gelled waxy crude oils”. *Fuel*, Vol. 222, pp. 444–456.

Webb, E.B., Koh, C.A. and Liberatore, M.W., 2013. “Rheological properties of methane hydrate slurries formed from aot+ water+ oil microemulsions”. *Langmuir*, Vol. 29, No. 35, pp. 10997–11004.

Webb, E.B., Koh, C.A. and Liberatore, M.W., 2014. “High pressure rheology of hydrate slurries formed from water-in-mineral oil emulsions”. *Industrial & Engineering Chemistry Research*, Vol. 53, No. 17, pp. 6998–7007.

Webb, E.B., Rensing, P.J., Koh, C.A., Sloan, E.D., Sum, A.K. and Liberatore, M.W., 2012. “High-pressure rheology of hydrate slurries formed from water-in-oil emulsions”. *Energy & fuels*, Vol. 26, No. 6, pp. 3504–3509.

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