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INTERFACIAL RHEOLOGY OF CYCLOPENTANE HYDRATES

Marina Ribeiro Bandeira
Gustavo Alonso Barrientos Sandoval
Department of Mechanical Engineering, Pontifícia Universidade Católica do Rio de Janeiro, RJ, 22451-900, Brazil
marina_guidoval@hotmail.com
gsandoval@puc-rio.br

Monica Feijó Naccache
Paulo Roberto de Souza Mendes
Department of Mechanical Engineering, Pontifícia Universidade Católica do Rio de Janeiro, RJ, 22451-900, Brazil
naccache@puc-rio.br
pmendes@puc-rio.br

Adriana Teixeira
Leandro Saraiva Valim
Petrobras Research Center (CENPES), Petrobras Av. Horácio Macedo 950, Cidade Universitária, Ilha do Fundão, Rio de Janeiro, RJ 21941-598, Brazil
adriteix@petrobras.com.br
leandro.valim@petrobras.com.br

Abstract. *Gas hydrates are crystalline compounds physically resembling ice, where small molecules (guests) are trapped inside the water hydrogen-bonds (hosts). The cavities formed by these structures are generally occupied by external molecules such as low molecular weight hydrocarbon gases. The stabilization of the gas hydrate structures occurs due to the presence of these small substances known as hydrate formers through the weak van der Waals force. Hydrates are formed at low temperatures and moderate or high pressures. These conditions are, usually, attained in the offshore oil and gas drilling, production, and transportation processes. Therefore, hydrates can form within the flowlines causing a parcial or total block of the pipeline, resulting in economic and safety problems. Hydrates formation occurs at the water-hydrocarbon interface, therefore, it is important to investigate the kinetics of hydrate systems in this region. One approach which permits conducting that investigation is through the interfacial rheology technique, then, the objective of the present work is to bring different insights about the hydrate film dynamics. The experiments were conducted using cyclopentane as a guest molecule since this hydrocarbon forms hydrates under atmospheric pressure, and accessible temperatures. Moreover, it forms the crystalline structure II, which is the same found in production lines of the oil and gas industry. Oscillatory tests were performed to obtain the rheological response at the interface, using the commercial rheometer DHR-3 and the double-wall ring geometry, which is placed at the interface between water and hydrocarbon. To obtain an accurate temperature control of the system, a homemade brass base was employed in the tests. The results are depicted through the interfacial dynamic modulus G' and G" for different oil phases, composed of primol and cyclopentane: (I) pure cyclopentane, (II) 90% cyclopentane and 10% primol, (III) 80% cyclopentane, and 20% primol. The tests aim to evaluate the effect of adding primol on the kinetics of hydrate film formation. In all cases, hydrate formation is detected by a stochastic growth of the interfacial storage modulus (G') with time. After that, G' reaches a plateau meaning that a stable hydrate film was formed. The results show that by increasing the concentration of Primol oil, a thinner hydrate film is obtained, which makes it suitable to be investigated through the shear interfacial rheology technique. The storage modulus decreases approximately one order of magnitude when the quantity of Primol is increased from 10% to 20%.*

Keywords: *hydrate, cyclopentane hydrate, interfacial rheology, double wall ring.*

1. INTRODUCTION

Clathrate hydrates are composed by water and low molecular weight hydrocarbon gases (C1–C4) or other gases such as H_2, N_2, CO_2, and H_2S. These hydrate formers are trapped inside "cages" of hydrogen-bonded water molecules at low temperatures and high pressures (Zylyftari *et al.*, 2014). Hence, they are particularly prevalent in oil and gas transportation in multiphase flowlines. The formation, agglomeration, and accumulation of hydrates can block transportation lines, increasing production costs, damaging equipment, reducing the efficiency of the extraction process, compromising the safety of the operations, and harming the marine environment (Lee *et al.*, 2014). For these reasons, the research on hydrates has been expanded rapidly (Sloan, 2004).

Hydrate's formation begins when the system reaches a point within the hydrates thermodynamic stability region. This occurs at the interface between the water and hydrocarbon fluid (oil or gas), forming a shell structure around the water/oil droplets (emulsified in oil/water) (Wilson, 2010). This process at interface is called nucleation, where the first agglomerates emerge and disperse to achieve a critical size for continued growth, at any temperature below the hydrate dissociation temperature. The time elapsed during the entire nucleation process is called induction time and includes the onset of growth up to the point at which hydrates are first macroscopically detected since it occurs on a small size scale to be detected (Bishnoi *et al.*, 1996).

Usually, gas hydrates are subdivided into three structures. The structure I is formed from a mixture of water and small hydrocarbon molecules, such as methane and ethane. The structure II is formed by larger hydrocarbons such as propane, butane, and cyclopentane. They are typically found in oil and gas pipelines. Also, the structure H is formed from a combination of, at least, two cavities: small cavities (for gases with lower molecular weight) and large cavities (to trap cyclopentane or cyclooctane, for example) (Sloan and Koh, 2008).

As mentioned, low temperatures and high pressures are required to form hydrate. However, cyclopentane (C5 – cyclic) hydrates are formed at atmospheric pressure and temperature up to 7 ºC (Nakajima *et al.*, 2008). Due that cyclopentane (CP) hydrophobic properties, the formation of hydrate with this hydrocarbon mimics the mass transfer process found in real applications. Furthermore, the structure of the CP hydrate formed is type II, which is similar to the hydrate structure obtained with natural gas (Raman *et al.*, 2016). Therefore, cyclopentane hydrates are a model system for gas hydrates since the conditions are easily attainable in the laboratory.

As hydrate nucleation happens at the interface between water and hydrocarbon, where the Gibbs free energy of nucleation is lower (Radhakrishnan and Trout, 2002), it is important to investigate the mechanics of hydrate systems using interfacial rheology to directly measure the hydrate film dynamics (Zylyftari *et al*., 2014). The proposed approach is to study the response of complex fluid-fluid interfaces in kinematically simple deformations to obtain material functions. This method describes the functional relationship between the deformation of the interface, the stresses exerted in and on it and the resulting flows in the adjacent fluid phases, and is divided in two groups: shear and dilatational measurements. The first is based on the interfacial shear in which the interfacial area is kept constant. On the other hand, dilatational rheology is based on expansion/contraction of the interface at constant rate keeping the interfacial shape unchanged (Ravera *et al*., 2010). With this technique it is possible to measure the viscoelastic characteristics of a film interface. For example, in oscillatory experiments, the strain or stress is sinusoidally varied at an angular frequency while the storage (G') and the loss moduli (G'') are acquired (Pelipenko *et al*., 2012).

The main objective of this work is to obtain the shear rheological response at the interface during hydrate films formation. The double-wall geometry (DWR) is used for the interfacial measurements, and a protocol for the accomplishment of the hydrate formation experiments using this geometry is established. In this way, a set of rheometric experiments was carried out to characterize the kinetics of hydrate films formation.

2. EXPERIMENTAL SECTIONS

2.1 Materials

All experiments were performed usin deionized water, purified through reverse osmosis and obtained from the Gehaka OS 10 LX system, and pure cyclopentane (≥ 98%) from Sigma-Aldrich. Primol oil was added in some experiments to evaluate its effect on the kinetics of hydrate films formation. This oil is highly refined, composed of saturated aliphatic hydrocarbons. For each test, it was used 19.6 g of deionized water and (I) 7 ml of pure cyclopentane, or (II) 7 ml of a mixture of 90% cyclopentane and 10% Primol, or (III) 7 ml of a mixture of 80% cyclopentane and 20% Primol. The oil phase composed by cyclopentane and Primol oil was mixed with the add of a magnetic stirrer at 1000 rpm, and temperature of 30 ºC for 5 minutes.

2.2 Methods

The rheometric experiments were carried out in the DHR-3 rheometer from TA Instruments, which is a hybrid rheometer with stress control. The rheometer includes a Peltier system that provides an accurate temperature control during the experiments, and, thereby, allows the development of hydrates.

The geometry used to perform all the measurements was the "double wall ring" (DWR) interfacial geometry. A brass cell with double wall that sits on top of the Peltier plate of a rotational rheometer was used together with the double wall ring made of Pt/Ir. As brass cell is a good thermal conductor, the temperature imposed by the Peltier plate can rapidly be transmitted to the rest of the system (Figure 1).

Figure 1. Brass cell.

The cross section of the ring is square-shaped (Figure 2) with a sharp edge to create, as much as possible, a planar interface. The sample is contained in a trough and the ring is positioned at liquid/liquid interface and connected to the rheometer. To create pinning of the interface and reduce meniscus effects at the inner and outer sides of the trough, stepwise edges are present and mark the height level of the lower fluid (deionized water).

An insulation cap is used to minimize heat transfer from the surroundings and to hold the brass cell fixed and centered within the Peltier plate. Furthermore, a cover for humidity control is used, and to intensify its performance, silica beads were added, which absorbs condensed moisture.

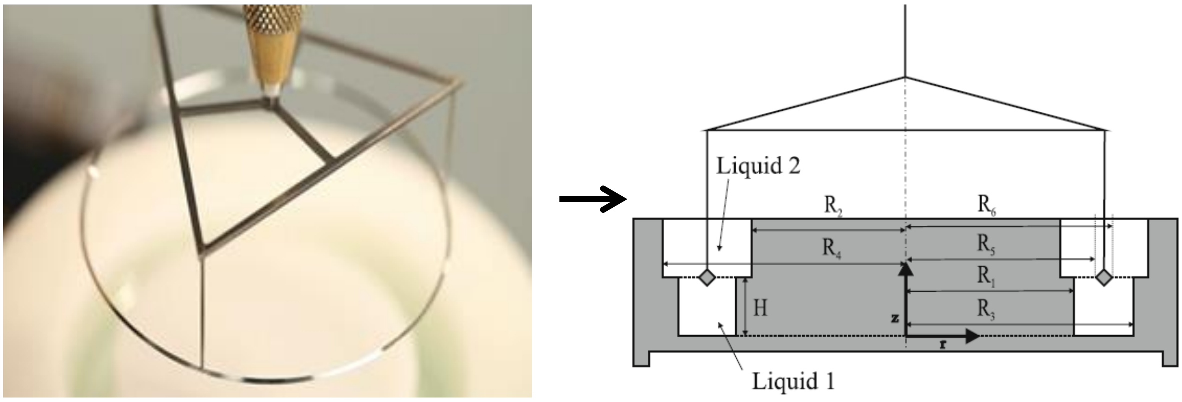

Figure 2. Double wall ring and its cross section view (Steven Vandebril *et al.*, 2009).

2.3 Measurement Protocol

Initially, 19.6 g of water is cautiously loaded to the brass cell using a graduated pipette, then, a temperature conditioning step is applied to the water. Initially, to ensure that all experiments start at the same temperature, the temperature was stabilized and conditioned at T_{cond} = 20 ºC for 10 minutes, as indicated in the 1st step of Fig. 3.

In the second step, water is cooled down from T_{cond} = 20 ºC to an initial temperature (T_i) of −10 ºC at a rate of −2.5 ºC/min. Then, the temperature is held at T_i = −10 ºC for 10 minutes to assure that the entire sample solidifies (third step of Fig 3). This stage is necessary because nucleation rates significantly increase when the water has been previously frozen, as indicated by Zylyftari *et al.*, (2013).

In the fourth stage, the temperature is increased to a final value (T_f) of 1 ºC at a rate of 5.0 ºC /min. This final temperature remains constant until the end of the experiment. When the ice starts to melt and a thin film of liquid water appears, the double wall ring is placed at the surface and the cyclopentane (or the mixture of cyclopentane and primol) is added cautiously on top of water. So, the ring remains positioned at interface between the aqueous and oil phases.

Once the DWR and both the phases have been placed, the measurements start to be captured (fifth stage). Time sweep tests were performed to track down the behavior of the elastic and viscous modulus of the water/cyclopentane interface. The strain applied was 0.05% at a frequency of 1 Hz (linear viscoelastic region).

An overview of the experimental temperature profile in each stage is exhibited in Figure 3.

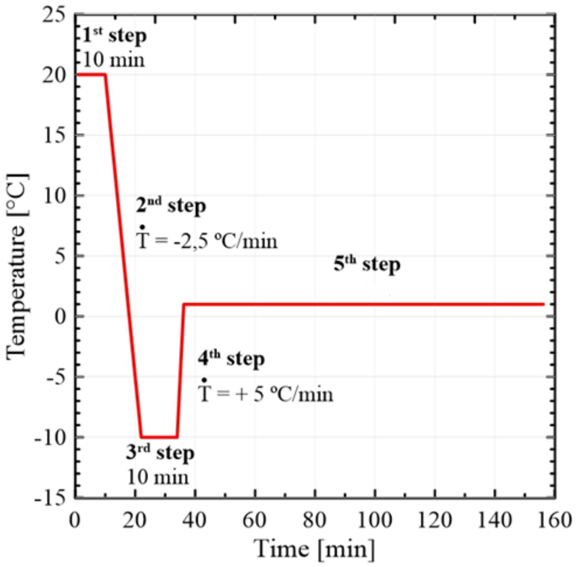

Figure 3. Experimental temperature cycle applied to the samples before the time sweeps tests.

3. RESULTS AND DISCUSSION

The interfacial films of hydrates were investigated through time sweep tests. The time t = 0 corresponds to the beginning of the test – 5th step showed in Fig. 3. Two curves are plotted for the same concentration of cyclopentane, one of them corresponds to a different run carried out with a different sample at the same experimental conditions, in order to assess the repeatability of the tests. So, the filled symbols indicate the first experiment of each sample and the empty symbols indicate the second run.

The experiments were performed at a final temperature of 1 ºC since this value ensures approximately 6 ºC below the hydrate equilibrium temperature. Three samples with different concentrations of cyclopentane were evaluated: pure cyclopentane, 90% of cyclopentane and 10% of primol, and finally, a sample with 80% of cyclopentane and 20% of primol.

A random and sharp increase in the storage modulus (G’) is observed at the beginning, for all tests, as it could be observed in Figures 4 to 6. This indicates the moment where hydrates formation occurred. A few seconds later, the increasing rate diminishes, and after the appearance of the hydrate structures, G’ reaches an asymptotic limit, indicating that a stable hydrate film was formed at the interface between water and cyclopentane (or mixture of cyclopentane and primol). Consequently, hydrate formation stops, and the film seems to not grow anymore. During the experiments, the existence of the hydrate film was visually confirmed, as it can be seen in Figures 4 (b) to 6 (b). All results reveal that these films are viscoelastic once they possess both storage and loss interfacial moduli. However, their elastic nature supersedes the viscous response, indicating a more solid-like material.

Despite hydrate formation is a stochastic phenomenon, it was observed that the hydrate formation for all the concentrations studied occurred during the first 600 s of the experimental time, in addition, a few discrepancies was noted with the repeatability tests.

Figure 4 (a) presents a time sweep test for pure cyclopentane. The elastic modulus (G’) stabilizes around 16 N/m, while the viscous modulus (G’’) was between 0.2 N/m and 0.3 N/m. The effectiveness of these results could be confirmed, as it presents very similar values with the repeatability test. However, it is worth mentioning that hydrate crystals grow abundantly in the DWR as well as in the brass base during the time sweep test (Figure 4 (b)). Probably, the larger amount of hydrate formed is due the higher cyclopentane concentration. Usually, for these cases, the ring loses most of its contact area with the interface, as large amount of hydrate crystals migrate to the brass cell walls.

Primol oil was added to the oil phase to evaluate its effect on hydrates formation. Initially, a mixture of 90% of cyclopentane and 10% of Primol oil was assessed, and as noted in Fig. 5(a), G’ reached a lower value when comparing with the one obtained for pure cyclopentane. The value achieved by G’ for the mixture was around 13 N/m, while G’’ stabilized between 0.3 N/m and 0.4 N/m. Both tests have a good repeatability, as shown in Figure 5. Figure 5 (b) also shows that less migration of hydrate to the brass cell occurred. In this case, most of crystals remained concentrated over the ring.

Another experiment with a mixture of 80% of cyclopentane and 20% of primol oil was conducted as show in Figure 6 (a and b). The measurements of the moduli value were very similar to the previous case (90% of CP and 10% of Primol oil), with G’ reaching an asymptotic limit around 13 N/m and G’’ was approximately 0,4 N/m. However, the hydrate crystals film did not migrate to the brass cell, remaining, mainly, at the interface (Figure 6 (b)).

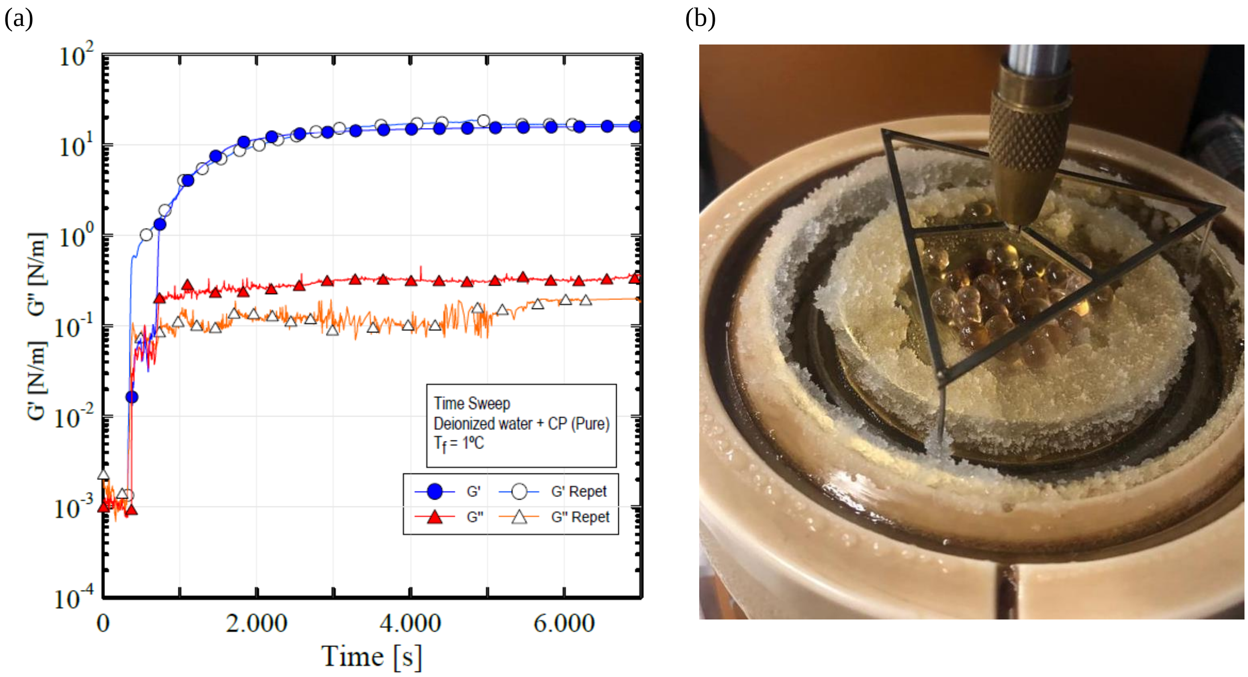

Figure 4. (a) Time sweep outcome for water/pure cyclopentane interface at T_f = 1 ºC. (b) Hydrate formation in the geometry.

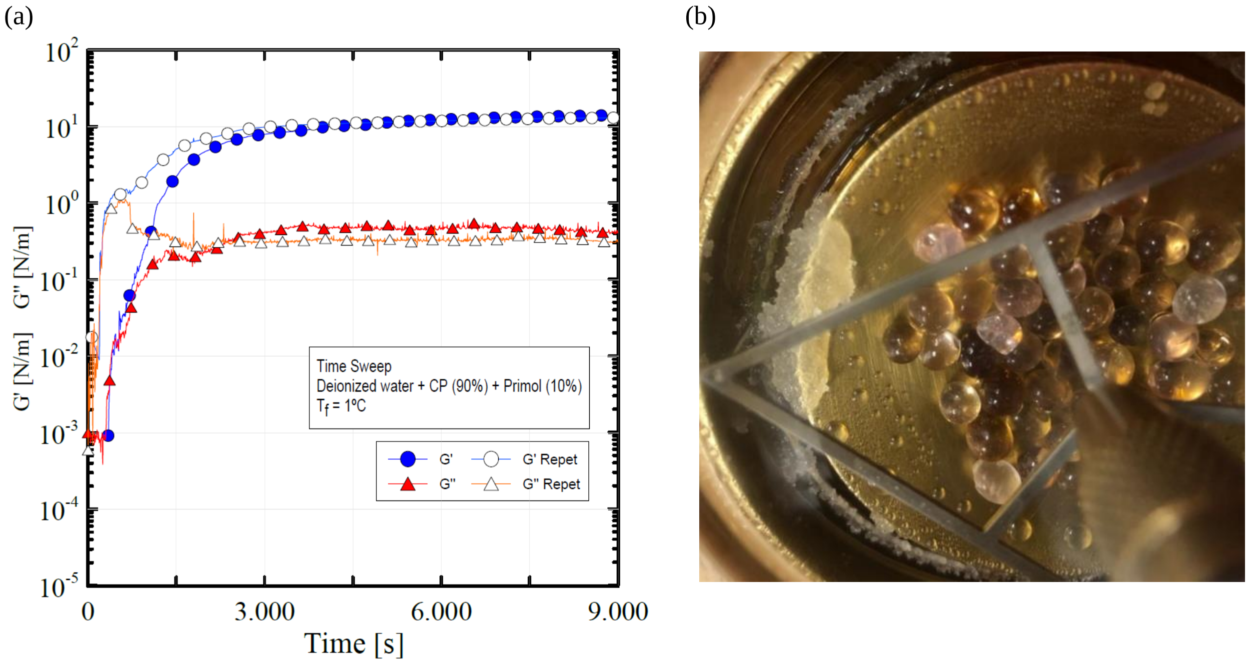

Figure 5. (a) Time sweep outcome for water/ 90% cyclopentane and 10% primol interface at T_f = 1 ºC. (b) Hydrate formation in the geometry.

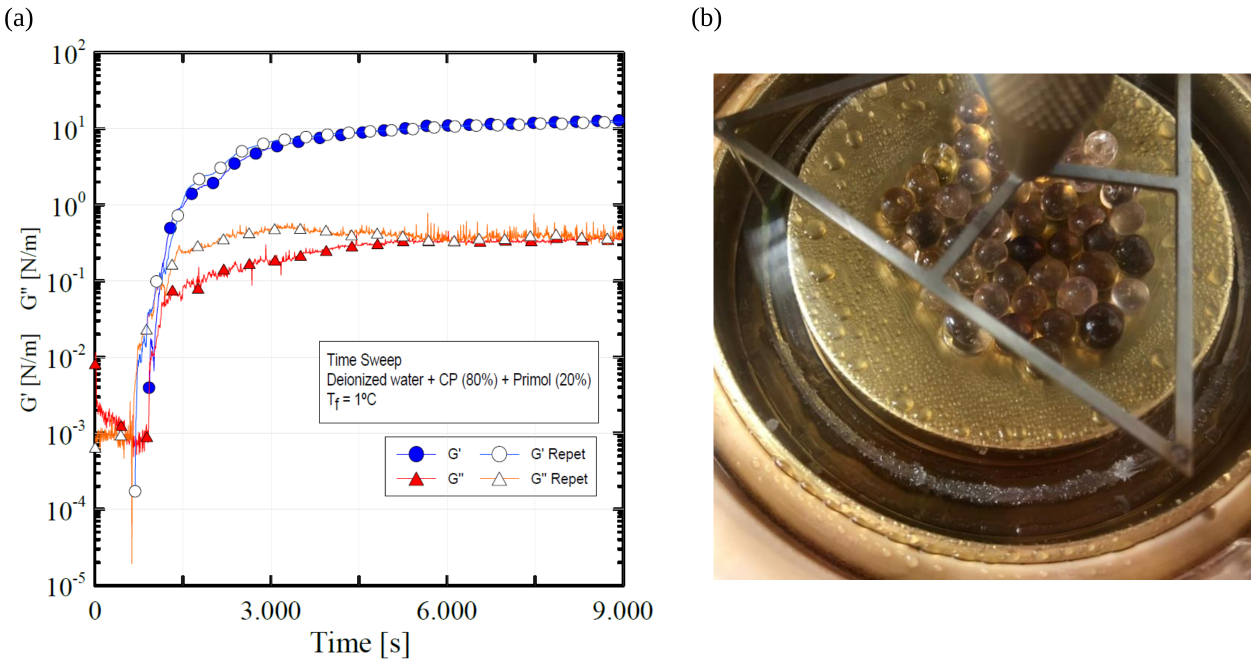

Figure 6. (a) Time sweep outcome for water/ 80% cyclopentane and 20% primol interface at T_f = 1 ºC. (b) Hydrate formation in the geometry.

4. CONCLUSIONS

Time sweeps experiments at the water/hydrocarbon interface were conducted for different concentrations of cyclopentane at the final temperature of 1 ºC and atmospheric pressure. An assemble composed by both a DWR geometry and a home-made brass cell was used to perform the experiments. The results obtained show good repeatability despite hydrates be a stochastic phenomenon. However, large amounts of hydrate were noted around the cell walls when only pure CP was assessed in the oil phase. For this case, most of the hydrate's crystal migrate from the interface and the DWR lost part of its contact area with the water/CP interface. To investigate this effect of hydrate migration, Primol oil was added to the oil phase as showed in Figs 5 and 6. When 10% of Primol oil was added to the oil phase, the elastic modulus was reduced from 16 to 13 N/m, and less amount of hydrate formation along the walls cell was noted. Hydrate's migration was avoided even more when 20% of Primol oil was added to the oil phase, and a desired hydrate film was identified at the water/hydrocarbon interface. Probably, the addition of Primol oil to the hydrocarbon phase hampers that large amount of CP to be captured and retained by the water hydrogen-bond.The findings reported can be useful for further development and analysis of hydrates formation experiments.

5. REFERENCES

Bishnoi, P.; Natarajan, V., 1996. Formation and Decomposition of Gas Hydrates. Fluid Phase Equilib. 117, 168−177.

Lee, B.; Koh, C.; Sum, A, 2014. Mechanism of Cohesive Forces of Cyclopentane Hydrates with and without Thermodynamic Inhibitors. Ind. Eng. Chem. Res. 53, 18189−18193.

Nakajima, M.; Ohmura, R.; Mori, Y. H., 2008. Clathrate Hydrate Formation from Cyclopentane-in-Water Emulsions. Industrial & Engineering Chemistry Research, 47, 8933-8939.

Pelipenko, J.; Kristl, J.; Baumgartner, S.; Kocbek, P., 2012. Interfacial rheology: An overview of measuring techniques and its role in dispersions and electrospinning. Acta Pharmaceutica, 62(2):123–140.

Radhakrishnan, R.; Trout, B., 2002. A new approach for studying nucleation phenomena using molecular simulations: Application to CO2 hydrate clathrates. J. Chem. Phys., 117:1786–1796.

Raman, A. K. Y.; Venkataramani, D.; Bhagwat, S.; Martin, T.; Clark, P. E.; Aichele, C. P., 2016. Emulsion stability of surfactant and solid stabilized water-in-oil emulsions after hydrate formation and dissociation. Colloids and Surface A: Physicochemical and Engineering Aspects, 506, 607-621.

Ravera, F.; Loglio, G.; Kovalchuk, V. I., 2010. Interfacial dilational rheology by oscillating bubble/drop methods. Curr. Op. Coll. Int. Sci. 15, 217–228.

Sloan, E. D, 2004. Introductory overview: Hydrate knowledge development. American Mineralogist, 89, 1155-1161.

Sloan, E.D. and Koh, C.A., 2008. Clathrate Hydrates of Natural Gases. Third Edition. Chemical Industries-New York Then Boca Raton-Marcel Dekker Then CRC Press-, 119.

Vandebril, S.; Franck, A.; Fuller, G. G.; Moldenaers, P.; Vermant, J. A double wall-ring geometry for interfacial shear rheometry. Research Gate 2009, 49:131–144.

Verwijlen, T.; Imperiali, L.; Vermant, J., 2014. Separating viscoelastic and compressibility contributions in pressure-area isotherm measurements, Adv. Colloid Interface Sci. 206, 428–436.

Wilson, P.; Haymet, A, 2010. Hydrate formation and re-formation in nucleating THF/water mixtures show no evidence to support a memory effect. Chem. Eng. J. 2010, 161, 146−150.

Zylyftari, G.; Ahuja, A.; Morris, J., 2014. Nucleation of cyclopentane hydrate by ice studied by morphology and rheology. Chemical Engineering Science, 116:497–507.

Zylyftari, G.; Lee, J. W.; Morris, J. F. Salt effects on thermodynamic and rheologicalproperties of hydrate forming emulsions. Chemical Engineering Science 2013, 95, 148–160.