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Interfacial Rheology as an Innovative Approach to Investigate Hydrate Formation and Inhibitors

Gustavo A. B. Sandoval[1], Marina R. Bandeira[2], Mônica F. Naccache[3], Paulo R. de Souza Mendes[4], Adriana Teixeira[5], and Leandro Valim[6]
[1]Wood Group Engineering and Production Facilities, Brasil LTDA *gustavo.sandoval@woodplc.com
[2,3,4]Department of Mechanical Engineering, Pontifícia Universidade Católica do Rio de Janeiro, Brazil.
[5,6]Petrobras Research Center (CENPES), Rio de Janeiro, Brazil.

Abstract

Hydrates, resembling ice-like solids, form when light hydrocarbon molecules and water combine in a specific ordered structure, predominantly at the water-hydrocarbon interface. This study investigates the role of interfacial rheology in hydrate formation using a rotational rheometer's "double wall ring cell" for precise temperature control. Cyclopentane serves as the hydrate former, facilitating experimentation under atmospheric pressure and various temperatures. By manipulating temperature and hydrocarbon concentrations, this research focuses on ice crystal involvement in hydrate formation initiation. Interfacial elastic and viscous moduli are determined through strain sweeps post-saturation, elucidating hydrate film rigidity and mechanical response. Tests with thermodynamic inhibitors like sodium chloride and monoethylene glycol demonstrate considerable extension in induction time.

Keywords

Hydrates; Interfacial Rheology; Thermodynamic Inhibitors

Introduction

Given that hydrates originate at the water-hydrocarbon interface, employing interfacial rheology offers a logical approach to understanding their behavior. This analysis can encompass both dilatational techniques [1 - 3] and shear methods maintaining constant area [4]. Leopércio et al. [5] presented pioneering work utilizing shear rheology with constant area, focusing on hydrate film growth kinetics. Their study utilized a modified double wall ring cell for interfacial moduli measurements, proving effective in temperature control of the water/hydrocarbon interface. The sensitivity of interfacial moduli measurements in indicating hydrate growth was verified [5], laying the groundwork for our experimental design.

Our study employs a direct approach to probe the mechanics of hydrate systems, utilizing interfacial rheology to directly measure hydrate film mechanical behavior. The pivotal role of the interface in hydrate nucleation and growth underpins this premise. Cyclopentane was deliberately chosen as the hydrate-forming substance due to its unique properties, including immiscibility with water and its capability to form hydrate structure II, akin to natural gas hydrates, under ambient pressures and readily achievable temperatures. Post-saturation of the hydrocarbon/water interface by hydrates, strain sweeps are conducted to evaluate interfacial elastic and viscous moduli, scrutinizing mechanical response and fragility of hydrate films.

Furthermore, our study extends its scope by testing two common thermodynamic hydrate inhibitors. This additional step aims to compare induction times of hydrates in the presence and absence of inhibitors.

Methodology

Materials

All experiments were performed using deionized water (DW) and pure cyclopentane (CP) (≥ 98%) from Sigma-Aldrick. Primol oil (PO) was introduced in some experiments to assess its impact on the kinetics of hydrate film formation. This highly refined oil consists of saturated aliphatic hydrocarbons and has been previously utilized in other studies (Sandoval et al., 2021; Rebello et al., 2023) [6, 7]. In each test, 19.6 g of deionized water was used along with one of the following three options: [I] 7 ml of pure cyclopentane, [II] 7 ml of a mixture containing a volumetric percentage of 90% cyclopentane of the total volume of the solution (vCP/vtotal) and 10% Primol oil (vOP/vtotal), or (III) 7 ml of a mixture containing 80% cyclopentane (vCP/vtotal) and 20% Primol (vOP/vtotal). To prepare the oil phase, which consisted of cyclopentane and Primol oil, the two components were mixed using a magnetic stirrer at 1000 rpm for 5 minutes while maintaining a temperature of 30 ºC.

In experiments involving inhibitors, thermodynamic hydrate inhibitors (THIs) were incorporated. For the analysis, the trials employed solutions, with one containing sodium chloride (NaCl) dissolved in deionized water, and the other comprising monoethylene glycol (MEG) dissolved in deionized water. In both cases, a 7 ml volume of cyclopentane was employed as the oil phase. The concentration of these inhibitors varied in each experiment and will be thoroughly detailed in the results section.

Methods

The mechanical shear properties of hydrate films were measured by using a stress-controlled Discovery Hybrid Rheometer (DHR-3) from TA Instruments (see Fig.1 [a]) coupled with a double wall-ring (DWR) made of Pt/Ir, and a custom-made brass cup to place the water and oil subphases (see Fig. 1 [b]). This brass cup is a good thermal conductor, therefore, the temperature imposed by the Peltier plate can rapidly be transmitted to the rest of the system. The physical dimensions of the DWR geometry are extensively described in the TA instruments manual and have also been detailed by Vandebril et al. [8].

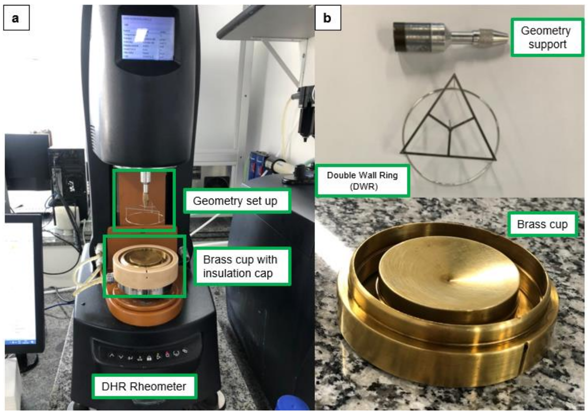

Figure 1. Overview of the DHR Rheometer. [a] Total view of the rheometer with the geometry setup attached to the instrument head. [b] Details of the accessories used in the rheological tests.

The DWR has a square-shaped cross-section with a precisely sharp edge, strategically designed to create a nearly planar interface. The sample is enclosed in a trough, and the ring is precisely positioned at the liquid/liquid interface and connected to the rheometer. To ensure accurate measurements and minimize meniscus effects at the inner and outer sides of the trough, stepwise edges are present and mark the height level of the lower fluid (aqueous phase). Before each run, the interfacial rheology testing platform is meticulously assembled. The brass cell is securely mounted and centered on the DHR-3 Peltier Plate, held in place by the insulation cap that is employed to minimize heat transfer from surroundings. To further enhance humidity control and avoid moisture interference, a humidity control cover is utilized, and silica beads were added to absorb any condensed moisture, thereby optimizing its performance.

Measurement protocol

Initially, 19.6 g of aqueous phase was carefully loaded into the brass cup using a graduated pipette. To ensure consistent starting conditions for all experiments, the temperature was stabilized and conditioned at Tcond = 20 ºC for 10 minutes, as shown in the first step of Figure 2. In the second step, the aqueous phase was cooled from Tcond = 20 ºC to an initial temperature of -10 ºC at a rate of -2.5 ºC/min. This temperature was maintained constant in the system for 12 minutes to allow the entire sample to solidify, as indicated in the third step of Figure 2. In the fourth stage, the temperature was raised to a final value of 1 ºC at a rate of 5.0 ºC/min. The final temperature is held constant for the rest of the experiment. The double wall ring was carefully placed at the interface when the ice was melted in the thin film of liquid water that appeared on the top of the phase. This occurred just after the 5th step (specifically, after 5 min when the final temperature evaluated was 1 °C, as indicated in Figure 2). Then, the oily phase (a mixture containing cyclopentane) was cautiously added on the top of the aqueous phase. Once the DWR and both phases were in place, measurements were initiated (fifth step in Figure 2).

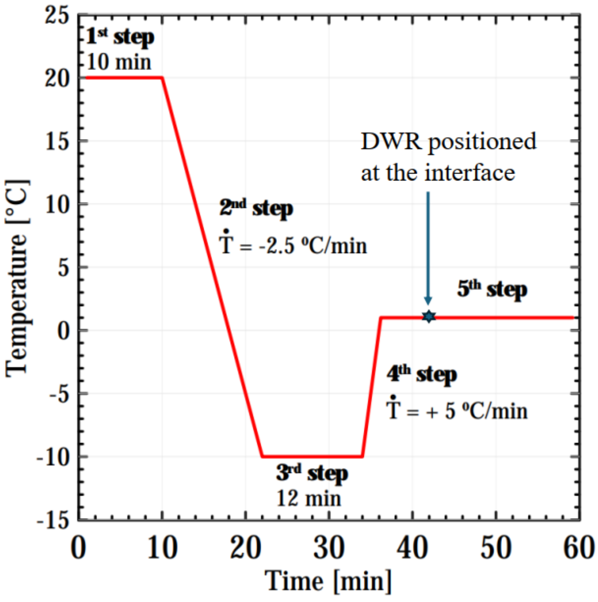

Figure 2: An experimental temperature cycle was applied to the samples both before (from the 1st to the 4th step) and during (at the 5th step) the tests measurement.

Results and Discussion

Initially, various preliminary experiments were conducted to determine the appropriate conditions (concentrations of the oily phase and temperatures) of our set up to run the tests. The results obtained using the time sweep approach are depicted in Figure 3. Those experiments were performed with a constant strain amplitude of 0.05% and a fixed frequency of 1 Hz within the linear viscoelastic region while the values of dynamic moduli were recorded over time. The time "t = 0" in Figures 3,4, and 4 corresponds to the beginning of the measurements, fifth step, as shown in Fig. (2).

Figure 2 shows the results obtained using an oily phase concentration of 80% CP (vCP/vtotal) and 20% PO (vOP/vtotal) at a final temperature of 1 ºC. After initializing the tests, before hydrates formation, values of G' and G'' lower that 1x10-3 N/m were measured by the rheometer in the time sweep tests. These data represented the measurements at the liquid interface between the oily and aqueous phases and were not taking into consideration because they were close or out the lower measuring geometry window. Then, during the first hour of those measurements, the hydrate formation through this methodology was readily observable when a distinctive abrupt rise in both G' and G'' was noticed, as illustrated in Figure 3. As observed, both modules grow, at least, 3 orders of magnitude during the formation of hydrates. This abrupt increase serves as a clear experimental indication of the moment when hydrate formation initiates, and the sustained growth and agglomeration of the hydrate crystals is happening. In general, the elastic modulus is associated with material stiffness. Therefore, a notable rise in G' serves as an indication of hydrate formation, given that hydrates are solid crystals known for their inherent rigidity, surpassing that of the surrounding fluids. In the sequence of experiments this occurs precisely when the elastic behavior of the sample overlaps the viscous one – the material has a predominant solid-like behavior. The increment on G'' could be associated with the increasing in the liquid viscous behavior caused by the presence of disperse tiny hydrate particles on it (see Figure 4).

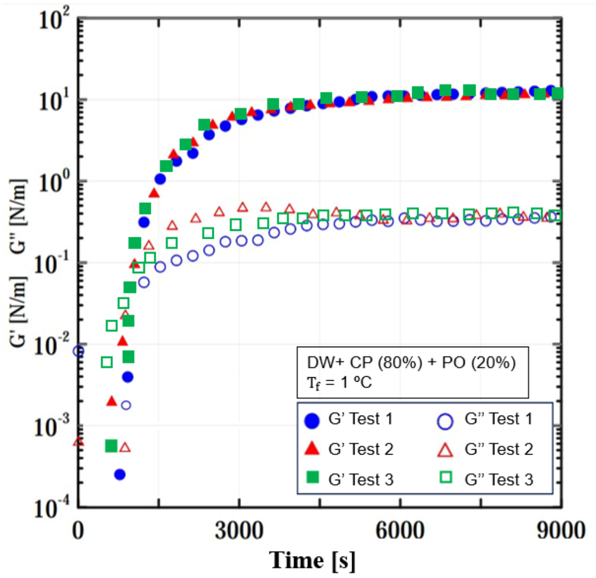

Figure 3: Time sweep tests – Moduli outcome for water and 80% CP and 20% PO at Tf = 1 ºC.

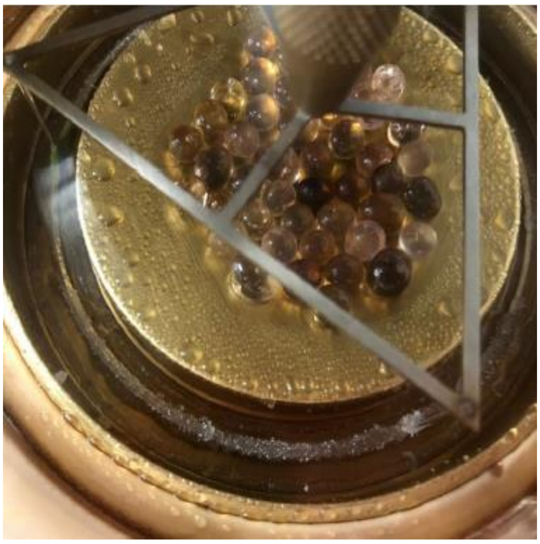

Figure 4: Hydrate formation at the geometry for water and 80% CP and 20% PO at Tf = 1 ºC.

Thermodynamic Inhibitors assessment

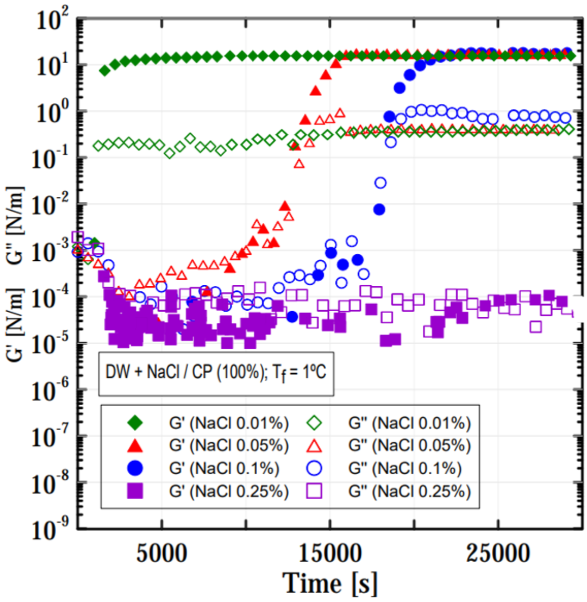

Figure 5: Effect caused on the induction time and moduli of the hydrate film by the addition of NaCl at Tf = 1 ºC.

In the initial inhibitor test, NaCl was added to deionized water at a concentration of 0.01% by mass of the final solution. Figure 5 illustrates the results of time sweep tests. Maintaining 100% CP concentration ensured accurate analysis, avoiding potential delays caused by Primol oil. At 0.01% NaCl, the induction time was around 1000 seconds, with an elastic modulus stabilizing at approximately 15 N/m. Increasing NaCl to 0.05% notably extended induction time to about 12,000 seconds, a twelvefold increase. Further delay occurred at 0.1% NaCl, reaching approximately 18,000 seconds. Growth times also lengthened compared to tests without NaCl. Despite delayed induction times, films formed with NaCl displayed similar elastic and viscous moduli, indicating the inhibitor primarily affected formation timing rather than final film properties. At 0.25% NaCl concentration, complete inhibition of hydrate formation was observed within the assessed period, as depicted in Fig. 5.

Monoethylene glycol (MEG), commonly used in the petroleum industry to prevent hydrate formation, alters thermodynamic conditions by lowering water's freezing point, hindering hydrate crystal formation. The results obtained with this inhibitor are shown in Fig. (6). Initial tests with 0.01% MEG concentration showed a slight increase in induction time compared to tests without the inhibitor, suggesting minimal inhibition effect. At 0.05% MEG, a significant extension in induction time to approximately 14,000 seconds was observed, indicating interference with hydrate nucleation without notable alteration in final material properties. Increasing MEG to 0.075% completely prevented hydrate formation throughout the analysis, demonstrating effective inhibition. Interestingly, hydrate growth with MEG was abrupt, contrasting with the gradual growth observed with NaCl.

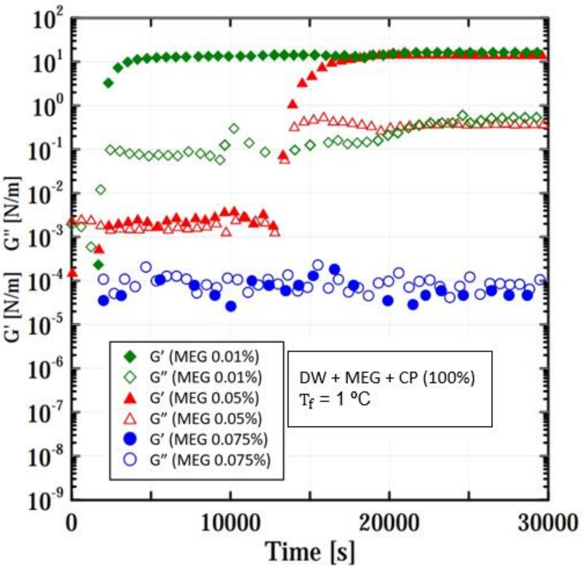

Figure 6: Effect caused on the induction time and moduli of the hydrate film by the addition of MEG at Tf = 1 ºC.

Conclusions

Our study contributes to advancing the fields of interfacial rheology and hydrate research by addressing a gap in understanding the interface between hydrocarbons and water during hydrate nucleation and growth. Utilizing a Double Wall Ring (DWR) for interfacial moduli measurements, along with a brass cup for precise temperature control, we explored the growth kinetics of cyclopentane hydrate films. Our findings highlight the sensitivity of interfacial moduli measurements in indicating hydrate growth, offering insights not achievable through observational approaches or traditional rheological studies burdened by emulsion mechanisms. This method shows promise for assessing hydrate growth kinetics under various conditions. Experiments with thermodynamic inhibitors, NaCl and MEG, revealed their efficacy in delaying or potentially inhibiting hydrate formation, depending on their concentrations. This understanding is crucial for managing hydrate-forming systems. However, it's important to note that inhibitor concentrations required for delaying or preventing hydrate formation may differ in bulk rheology studies. Our focus on interfacial rheology underscores its significance in elucidating hydrate dynamics and inhibitor effects.

Acknowledgments

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Responsibility Notice

The authors are the only responsible for the paper content (Arial 10).

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