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Gas Hydrate Formation and Agglomeration in Underinhibited Systems Containing Sodium Chloride, Ethanol and Ethylene Glycol

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Abstract
The formation of gas hydrates in underinhibited systems containing sodium chloride (NaCl), ethanol (EtOH) or ethylene glycol (MEG) was analyzed in this work in rheometers and in a balance cell. Initially, aqueous NaCl solutions containing 10% and 20% by mass of this salt were prepared. Considering the equilibrium curves of these two solutions, we calculated the necessary concentration of EtOH and MEG to generate curves close to those of NaCl. The calculated concentrations were then 16% EtOH and 19% MEG (curves like 10% NaCl), and 37% EtOH and 36% MEG (curves like 20% NaCl). The composition of the gaseous phase was a mixture of hydrocarbons, and the test pressure was 100 bar. Test temperatures were adjusted to have 10°C of subcooling. The results showed that, with increasing concentration of inhibitors, the induction time tends to increase, the relative viscosity tends to decrease, the rate of hydrate formation decreases, but the amount of hydrates formed at the end of each test varies a little. Another interesting point is to observe the fluids right after the end of the test, after the pressure cell has been depressurized. A hard plug of hydrates is observed in tests with pure water and no free water is observed, and in tests with inhibitors small pieces of hydrates and a lot of free water are observed. That is, for the same amount of hydrates, the formation process of the hydrate suspension seems to be different depending on the type and concentration of inhibitor present, and according to the observed results, it is suggested that the difference is in the morphology and on the size of the formed hydrates.

Keywords
Thermodynamic hydrate inhibitors; hydrate agglomeration; water salinity; underinhibited systems.

Introduction
Natural gas hydrates are clathrate-like compounds, with water molecules forming a cage surrounding a small molecule [1]. When water and small molecules, such as methane molecules, are placed in determined conditions of pressure and temperature, hydrates can be formed. These adequate conditions are, in general, low temperatures and high pressures, and such conditions are easily found during oil and gas production in an offshore environment. Hydrates can interrupt the multiphase flow of the produced fluids from a subsea well and pose an important flow assurance problem.

One way to avoid hydrate formation is by utilizing chemicals. Some chemicals, such as salts, alcohols, and glycols, change the gas hydrate equilibrium conditions, displacing the equilibrium curve to the left, where lower temperatures are necessary to form hydrates at a certain pressure, and this displacement is proportional to the inhibitor concentration. The chemicals that promote this equilibrium conditions displacement are called thermodynamic hydrate inhibitors (THI). Salts present in the produced water may help the inhibition strategy; alcohols and glycols can be added to the system and act as THIs. The thermodynamic basis for the evaluation of hydrates equilibrium conditions, with and without THIs, is well understood in the literature, and some studies show that the combined use of different THIs may be synergic [1; 2; 3].

Sodium chloride (NaCl), ethanol (EtOH) and ethylene glycol (MEG) are THIs, and if used in lower concentrations than necessary to inhibit the formation of hydrates under a given pressure and temperature condition, they will not completely inhibit the system. It is said that, in this situation, the systems are underinhibited for hydrates. It is important to remember at this point that the hydrate formation process can be considered as a classic crystallization process [1]. Thus, the nucleation

time and the growth rate of hydrate crystals can be associated with several driving forces, which are directly associated with the equilibrium conditions of hydrate formation. In this work, subcooling was considered as the driving force. At a given pressure, subcooling is the distance (in ^{o}C, for example) between the operating temperature and the hydrate equilibrium temperature. THIs shift the hydrate equilibrium curve to the left of a PT graph, thereby decreasing subcooling until the concentration of THIs is sufficient to completely inhibit hydrate formation at operating temperature, That is, the higher the concentration of THIs, the lower the subcooling until it is null.

In the field, situations can be found where the production system may be underinhibited for hydrates. In situations of a production shutdown, in a subsea oil well with no THI injection, where there are high pressures and low temperatures, the system is at risk of forming hydrates, since the saline composition of the produced water is generally not enough to inhibit them until the restart of the well. It is also possible to be underinhibited when there are problems in the alcohol or glycol injection system and the correct dosage is not injected.

Although it always seems like a bad condition, some studies show that operating in underinhibited systems, knowing the risks involved, can be attractive from a technical and financial point of view, being considered a form of hydrate risk management. In the literature, there are some studies addressing this issue, showing situations in which the potential for problems with hydrates may or may not increase when the system is underinhibited for a given type and concentration of THI.

Showing that underinhibited systems can worsen control over hydrate formation, a field test carried out at the Tommeliten gas field in the North Sea showed that the gas system without inhibitor formed less hydrate than the system containing a lower amount of methanol than the required for complete inhibition [4]. Yousif comments on these Tommeliten field test results and compares them with some laboratory tests [5]. He carried out tests with methanol and MEG at concentrations between 1 and 5% by mass, always at 40 ^{o}F and 900 psi (subcooling varying with the THI concentration), and observed that in this concentration range, the formation of hydrates was faster than in the system without inhibitor. He thus confirmed in lab the field test observations.

On the other hand, Hemmingsen et al report experimental studies with systems underinhibited with MEG and methanol, and indicate that this worsening may be related to the concentration of the inhibitor. In these studies, carried out in the presence of a ligth oil phase, they observed that the hydrate plugging potential of an underinhibited system increases up to a certain concentration of inhibitor (in this case, 10 to 15%), and then decreases [6]. In the presence of concentrations greater than 15% of MEG, they observed that the hydrates formed could be transportable. As the inhibitors are not incorporated into the crystalline structure of the hydrates, they accumulate in the aqueous phase that has not yet been converted, and their concentration in water increases, reducing the driving force of crystallization. They comment that the system becomes self-inhibited, from the concentrations mentioned above. At low concentrations, there is a greater interaction between the hydrate particles and the inhibitors, altering the wettability of the crystals in the presence of the oil phase, and promoting agglomeration. They observed that these behaviors are also confirmed in tests with the same subcooling, that is, it is not just a matter of the amount of hydrates formed and the driving force of crystallization.

Kim et al investigated, in an high pressure autoclave, the formation of hydrates in systems containing 10% and 30% MEG, at 100 bar and 4oC. In this case, subcooling in the test decreases with increasing THI concentration. They observed that with 30% MEG the induction time is longer, and the amount of hydrates formed is smaller, when compared to systems without inhibitor or with 10% MEG. They indicate that an underinhibited system with high concentrations of MEG, but still in concentrations lower than those necessary for complete inhibition, could have a low risk of blockage [7].

Performing tests in a flow loop, Lorenzo et al evaluated the deposition and agglomeration mechanisms of hydrates in the presence of MEG, in a gas system and in underinhibited conditions. They observed that, in concentrations of up to 30% of MEG, in tests with the same pressure and temperature, hydrate formation rates decreased linearly with increasing MEG concentration, as expected due to the decreasing driving forces. They also observed that, for MEG concentrations between 0% and 20%, hydrate formation rates were very similar when compared in the same subcoolings [8].

Some of these authors also commented on the possibility that different types and concentrations of THIs promote different hydrate morphologies. Kim et al observed the growth of hydrate crystals in subinhibition systems containing 5% MEG, or 5% methanol, or a mixture of MEG or methanol with 3.5% sodium chloride. Even at these low concentrations, they observed different crystal growth trends [9].

In this work we evaluated the process hydrates formation in different aqueous solutions by

rheology, using two different rheometers, and by using rock-flow cell [10]. Aqueous solutions with different concentrations of NaCl, EtOH or MEG were evaluated in 10 °C of subcooling, to decrease the influence of driving force on the crystallization process. The results of this study can help to understand what happens in the field, mainly in gas and water dominated systems. But they can also help to understand what happens in oil-dominant systems that produce water with different salinities and compositions, and the influence of adding other THIs to these systems. For example, Glenat et al evaluated, in systems containing oil, gas and saline water, the influence of up to 10% of NaCl present in the water on the transportability of hydrates. And they observed that transportability (measured through viscosity) increased with increasing salinity [11].

Methodology

Equipment

a) Rheometers: two different rheometers, with different measurement geometries, were used to evaluate the impact of hydrates formation in the viscosity of different aqueous solutions, as well as the water to hydrates conversion.

- R-1: A ThermoHaake MARS-III rheometer with its pressure cell and a solid vane geometry (Fig. 1). A gas reservoir, containing a pressure transducer and a temperature sensor, is connected to the pressure cell. The pressure cell also has a pressure transducer and a temperature sensor. Tests were done at constant pressure, and the water-to-hydrate conversion can be calculated through PT recordings from the gas reservoir and from the rheometer pressure cell [1]. This rheometer is located at CENPES, the Petrobras Research Center, in Brazil.
- R-2: A TA DHR-2 rheometer with its pressure cell and a hollow vane geometry (Fig. 2). A syringe pump is connected to the pressure cell. Tests were done at constant pressure, and the water-to-hydrate conversion can be calculated through recordings of gas consumed from the syringe pump. This rheometer is located at Professor Amadeu Sum's lab, at the Colorado School of Mines, in Golden, CO, USA.

b) Rock-flow cell: this equipment was used to visualize and follow different parameters during hydrates formation in different aqueous solutions. It is a stainless-steel pipe with 2" inner diameter and 3 feet in length, and the maximum operating pressure is 100 bar (Fig. 3). The main pipe is covered by a stainless-steel cooling jacket, which is connected to a chiller, to control the temperature. The pipe is positioned in a movable table so that a pendular movement can be applied. So, it can be moved back and forward, promoting shear inside the pipe. A gas reservoir is connected to the cell, but the tests were done in a constant volume type (the cell is isolated from the gas reservoir before the test starts). The cell pressure and the temperature of the tests are recorded, and then the water conversion to hydrates is calculated. This equipment is located at Professor Amadeu Sum's lab, at the Colorado School of Mines, in Golden, CO, USA.

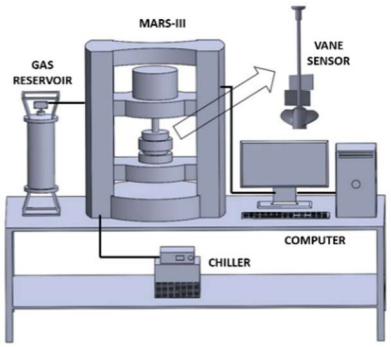

Figure 1. R-1: ThermoHaake MARS-III Rheometer setup and the solid vane measuring geometry for pressure cells used in the tests.

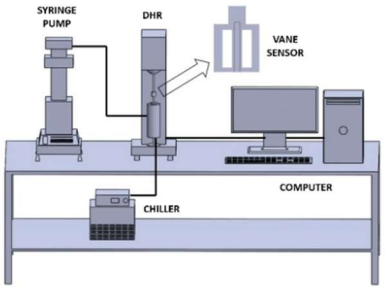

Figure 2. R-2: TA DHR-2 Rheometer setup, with pressure cell installed and the hollow vane used in the tests as the measuring geometry.

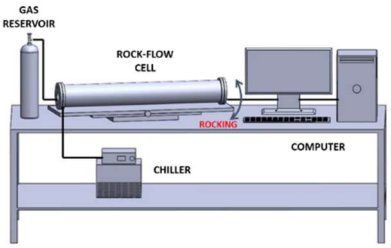

Figure 3. Scheme of rock-flow cell setup.

Materials

a) Gas mixtures: two different gas compositions were used in this work (mol%):

- NG1: methane (86.85%), ethane (10.07%), propane (2.02%), i-butane (0.05%), n-butane (0.04%), i-pentane (0.03%), n-pentane (0.02%), n-hexane (0.02%), carbon dioxide (0.40%) and nitrogen (0.50%). Supplied by White Martins (99%).
- NG2: methane (75%) and ethane (25%). Supplied by General Air (99%).

b) Aqueous solutions:

- sodium chloride (NaCl) was used to prepare 10 wt% and 15 wt% solutions (in deionized water) for the R-2 and the rock-flow cell tests.
- sodium chloride (NaCl), ethanol (EtOH), and ethylene glycol (MEG) aqueous solutions were prepared in the concentrations described in Table 1, for the R-1 tests. Each THI concentration was calculated per the NaCl 10% and 20% hydrates equilibrium curve considering the NG1 composition: the goal was to prepare EtOH and MEG solutions with the same hydrate equilibrium temperature at 100 bar, and do the tests in the same subcooling (Fig.4).
- NaCl was provided by Isofar (99,5%), EtOH (99%) and MEG (99%) were provided by Synth.

Table 1 – Temperature of tests and aqueous solutions concentration.

Test conditions at 100 bar T_{test} = T at 10 °C subcooling			
NG1			NG2
Pure water			Pure water
T_{eq} = 18 °C			T_{eq} = 19 °C
T_{test} = 8 °C			T_{test} = 9 °C
NaCl	EtOH	MEG	NaCl
10 wt%	16 wt%	19 wt%	10 wt%
T_{eq} = 14 °C			T_{eq} = 15 °C
T_{test} = 4 °C			T_{test} = 5 °C
20 wt%	37 wt%	36 wt%	15 wt%
T_{eq} = 7 °C			T_{eq} = 12 °C
T_{test} = -3 °C			T_{test} = 2 °C

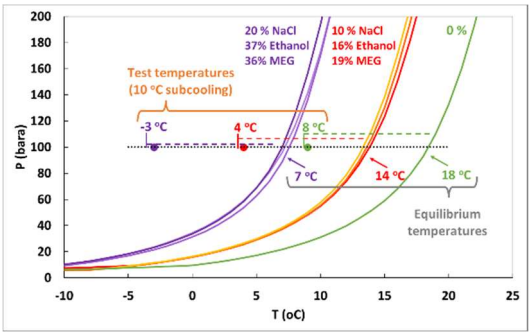

Figure 4 – Hydrate equilibrium curves for the different aqueous solutions and NG1 (Petrobras in-house software).

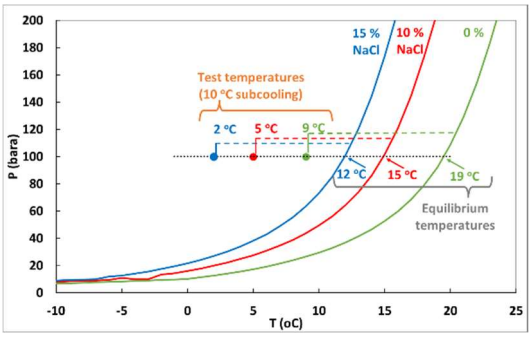

Figure 5 – Hydrate equilibrium curves for the different aqueous solutions and NG2 (Petrobras in-house software).

To identify the temperature tests in Table 1, at 100 bar, the information shown in Fig. 4 and Fig. 5 was considered. Test temperatures were defined as the temperature where each system is submitted to a subcooling of 10 °C.

Experimental procedures

a) Rheometers experimental procedure: The sample volume is added to the cleaned pressure cell, the measurement geometry is adjusted, the cell is closed, and then placed in the rheometer. The starting test temperature is selected in the chiller, the cell is pressurized, and the test starts following the steps in Fig. 6. The shear rate is constant during all the steps: 50 s^{-1} at the R-1, and 200 rpm at the R-2. Pressure is maintained constant in both systems. As both vanes were custom-made, and designed to promote efficient mixing in the system, which is critical to forming hydrates in rheometer tests, a correlation between the torque measured and the apparent viscosity was performed, using standard viscosity oils with known viscosities.

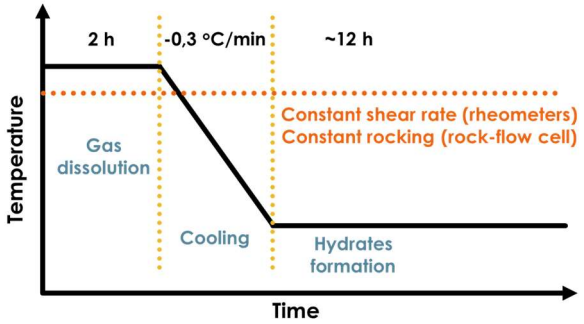

Figure 6 – Rheometers and rock-flow experimental procedure.

b) Rock-flow cell experimental procedure: The sample volume is added to the cleaned pipe, and the pipe is sealed. The starting test temperature is selected in the chiller. After cell temperature stabilization, the pipe is pressurized, and the test starts following the steps in Fig. 6. The rocking movement is constant during all the steps. The equipment is isolated and not connected to a gas reservoir during the test; so, the pressure varies during the tests, mainly during the cooling step and when hydrate is being formed, and the water-to-hydrates conversion is calculated according to this pressure variation.

Results and Discussion

Interfacial tension (solution:air) and density of all aqueous solutions were measured (Table 2). The interfacial tension was measured in a KSV 700 Tensiometer (DuNouy ring), and an AntonPaar DMA4500 Densitometer was used to measure the solution's density.

Table 2 – Physical characterization of aqueous solutions

Solution	Density (g/cm³)	Interfacial tension (mN/m)
Pure water	0.9998	71.4560
10 wt% NaCl	1.0676	74.6120
15 wt% NaCl	1.0990	76.0830
20 wt% NaCl	1.1303	77.5540
16 wt% EtOH	0.9300	40.5730
37 wt% EtOH	0.9700	30.4660
19 wt% MEG	1.0300	65.0390
36 wt% MEG	1.0600	63.0000

Figure 7 shows a typical result for all the hydrates tests performed in both rheometers. As illustrated in Fig. 6, in the first step, the temperature is kept at 40 °C. Then, the system is cooled to the test temperature and is maintained there for some hours (around 12 hours or more; enough time to observe some viscosity stabilization, if no blockage is observed). The viscosity is measured during all these three steps. In this example, the curve shows an abrupt increase during cooling, showing that hydrates were formed before achieving the desired temperature. In this case, hydrates started to form in a subcooling much lower than 10 °C (very close to the equilibrium temperature). Due to the characteristics of the vane, it is possible to observe some fluctuations in the measurements.

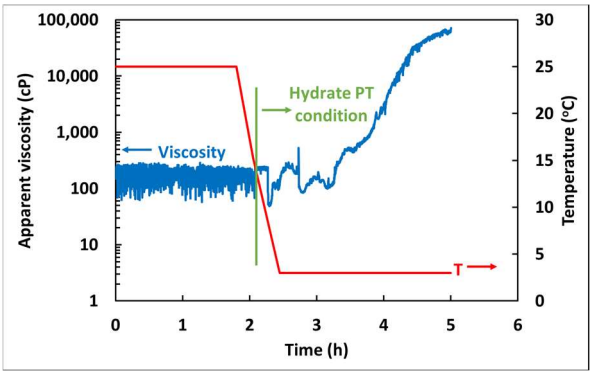

Figure 7 – Hydrate formation test in the 10% NaCl solution on R-2 (NG2, 100 bar). The green bar represents the moment of the entrance to the hydrate region.

Tests with aqueous solutions (Table 1) were done in both rheometers and similar viscosity curves to Fig. 7 were obtained for all of them. All tests were repeated at least two times and showed good repeatability. To analyze and compare the results of the hydrate formation process, viscosity plots were done. Fig. 8 shows some results obtained in R-2. In these plots, the zero time represents the time when hydrates started to form. The water conversion (%) was also calculated for the results shown in Fig. 8, considering the gas consumption registered by the syringe pump (Fig. 9) [1].

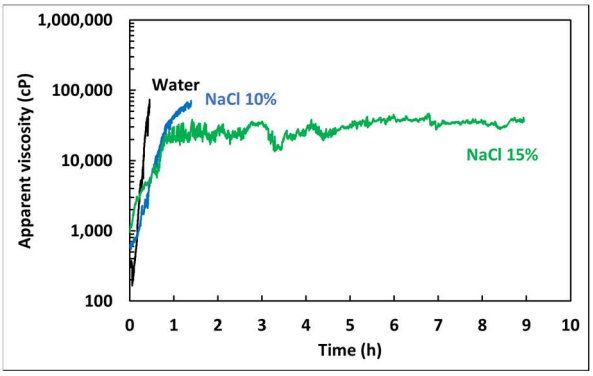

Figure 8 – Apparent viscosities of hydrate formation tests in water and in the NaCl solutions on R-2 (NG2, 100 bar, 10 °C subcooling). Details are in Table 1.

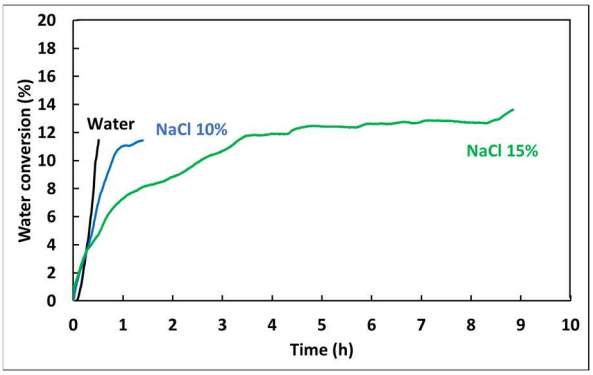

Figure 9 – Water-to-hydrate conversion (%) calculated for the tests illustrated in Fig. 8.

Besides the oscillations observed in the viscosity curves, it is possible to have a good comparison between them: hydrates formed in pure water showed a quick increase of the slurry viscosity and interrupted the movement of the rheometer. The same occurred with 10% NaCl solution, but the formation rate (described by the viscosity curve inclination) was a bit slower than the one with pure water. Finally, the slurry formed in the 15% NaCl solution didn't interrupt the rheometer measurement, and the measured viscosities were a bit lower than the previous ones.

Similar trends were obtained in the R-1 tests, with different brines in the same subcooling (Table 1). All the results obtained in R-1 tests are summarized in the following bar graphs. The relative viscosity, indicated in Fig. 10, corresponds to the viscosity of the slurry divided by the solution viscosity before the formation of hydrates. Results show that the relative viscosity is lower than the blank test for all tested solutions, with no clear difference or trend between the inhibitors solutions. A minor difference can be observed for ethanol solutions, with relative viscosities a little bit higher than the NaCl or MEG solutions.

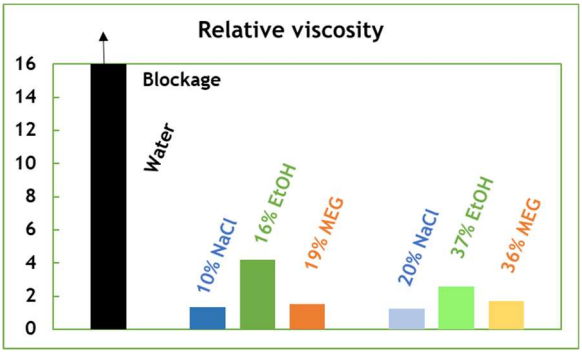

Figure 10 – Relative viscosity of hydrate slurries measured in the different aqueous solutions. R-1, NG1, 10 °C subcooling (Table 1).

Figure 11 shows the induction times of R-1 tests. Induction times of hydrates formation represent the time, inside the hydrate region, within no hydrates are observed. Or, in other words, the time when we observe the beginning of the hydrate formation process, considering the time inside the hydrate region. It is possible to observe that, for the lower concentration group, NaCl and ethanol show similar induction times to the blank system. They didn't show any influence on the induction time of hydrates formation. With 19% of MEG, the observed induction time was 3 times higher. Considering the solutions with higher inhibitor concentrations, it was observed that the induction time was again similar between NaCl and ethanol, but this time the values were higher than the blank test. Again, MEG solution showed higher induction times than the other two solutions. In spite of these results, as the hydrate crystallization is a stochastic event, it is important to look at these induction times results with care. Here we considered just the trends. To really consider them it is necessary to do more experiments and a statistical treatment of the results to have more representative numbers.

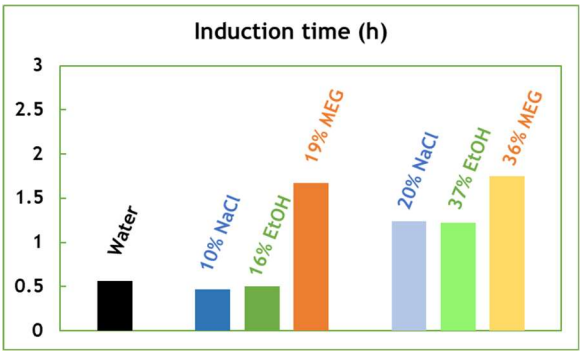

Figure 11 – Induction times of R-1 tests (NG1, 10 °C subcooling (Table 1).

Analyzing the water-to-hydrates (%) results for R-1 tests, it is possible to see in Fig. 12 a clear tendency in decreasing the conversion of water for all solutions, compared to the blank test. All the curves obtained with the different concentrations of inhibitors show lower conversion rates and lower conversion values than the test with water. Attention is drawn to the differentiated result of the MEG 36% solution, where the water conversion was around half of the other inhibitors solutions.

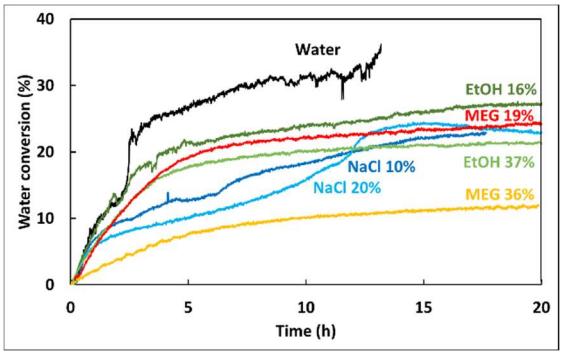

Figure 12 – Water-to-hydrate conversion (%) calculated for the tests in R-1 (NG1, 10 °C subcooling, Table 1).

Considering the results from Fig 12, it is possible to calculate the water conversion (%) in the first hour of hydrates formation. The results (Table 3) highlight the different behavior of MEG solutions in the kinetic steps of hydrates formation.

Table 3 – Observed induction times and initial water conversion rate for the tests described in Fig. 11 and Fig. 12.

Solution	Induction time (h)	% water converted / h (first hour)
Pure water	0.53	8.9
10 wt% NaCl	0.47	6.8
16 wt% EtOH	0.51	8.1
19 wt% MEG	1.67	5.5
20 wt% NaCl	1.24	5.8
37 wt% EtOH	1.22	5.7
36 wt% MEG	1.75	2.1

Comparing the viscosity (and relative viscosities) results obtained with R-1 and with R-2 rheometers, despite the different values observed, the trends were similar: even in the same subcooling, the presence of different thermodynamic inhibitors may have an influence on the hydrate formation process. Some differences in the results may be attributed to the different geometries adopted. The hollow vane (R-2) has the characteristic of no accumulation of hydrates between its blades, as the solid vane (R-1) has. This is a limitation of this type of geometry, and it is important to consider this features in the results analysis. Also, due to the different shear rates promoted by each geometry, in different equipment, and the non-newtonian characteristic of the hydrate slurries, it is expected to observe this difference in the hydrate slurries measured viscosities. But, despite all of that, it is possible to observe some trends when increasing the concentration of the different inhibitors.

At the end of each R-1 test, it was possible to do a quick cell depressurization keeping the test temperature. And then open the cell to try to have

some visual information (Fig. 13). It was very interesting to observe large hard chunks stuck to the vane for all tests with pure water. In the presence of salts, small soft pieces were obtained. And with MEG or EtOH, a few small and soft pieces were found immersed in a foam.

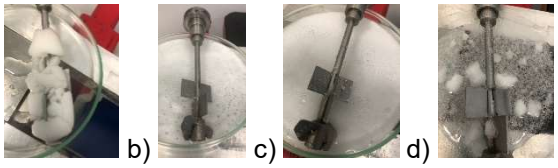

Figure 13 – a) pure water; b) EtOH 16% or 37%; c) MEG 19% or 36%; d) NaCl 10% or 20%.

Looking at these images and the previous results, it is possible to imagine that, in the presence of the inhibitors, the morphology of the hydrates is different from the system containing only water. And that, when depressurized, the hydrates formed in the presence of the inhibitors break down more quickly. Perhaps they are more porous hydrates, with more unconverted and inhibited water in their pores, or they are formed by smaller particles. It is important to remember that, when forming the crystalline structure of the hydrates, the additives do not participate in that structure and are concentrated in the aqueous phase that has not yet been converted. This fact changes the driving force of the crystallization process slowly, and it can change the morphology of the crystals that continue to form.

As described above, some tests with salt solutions and NG2 were done in the rock-flow cell equipment. The results are summarized in Fig. 14. In this equipment we have the visual information, due to a camera placed inside the pipeline, and the pressure and temperature recordings. In a different way from the rheometer's tests, the tests on the rock-flow cell were done in a constant volume method. Figure 14 shows a typical result obtained at this setup: a pressure curve showing its decrease during the cooling step, and another decrease when hydrates start to form.

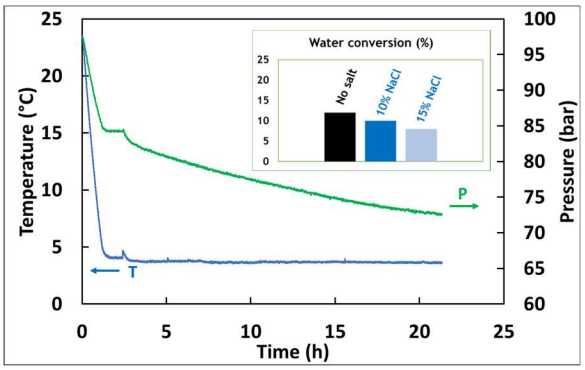

Figure 14 – Hydrates formation test with 10% NaCl solution at Rock-flow cell; NG2; attached, the water conversion results at 8 hours of test for the three different solutions.

The water-to-hydrate conversion was calculated for all the tests performed in this system, and is also part of Fig. 14. It is possible to note a similarity between these results and the results obtained in the rheometer tests: the water-to-hydrate conversion values are very close in all the tests, but it is possible to see a slight tendency to decrease with the increase of inhibitor concentration. Induction times also increased with the increase of NaCl concentration.

Figure 15 shows an image of the internal part of the rock-flow cell during one of the tests with pure water. It is possible to see some big pieces of hydrates in the bottom part of the cell, and also some hydrates deposited in the wall.

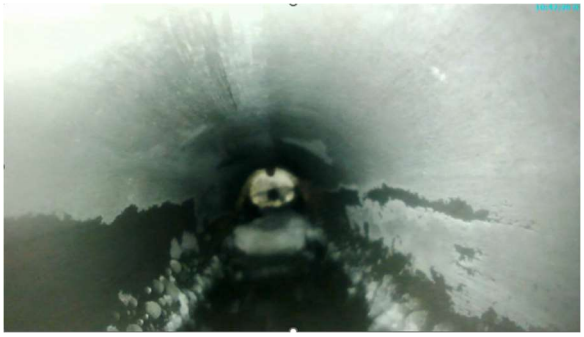

Figure 15 – Hydrates observed during the test with pure water in the rock-flow cell: hydrates in the bulk and deposited in the wall.

Conclusions

The results obtained in this work showed that there is a tendency to improve the transportability of the hydrates with the increase of the THIs concentration, in underinhibited conditions, even using different equipment.

As the tests were carried out at 10 oC subcooling, it was possible to minimize the effect of the decrease in the driving force with the increase in the concentration of inhibitors. Observing the tests carried out in each setup, the trends are similar in showing, for example, that by increasing the salinity of the water, the conversion of water into hydrates does not change much, the relative viscosity tends to decrease, and the induction time tends to increase.

To adjust the same test subcooling, the temperatures used were decreased, and certainly will not be found in the field. Therefore, the results obtained are more critical in relation to the process of hydrate formation, amount of hydrates formed, etc.. The objective was really to assess whether there was any influence that was independent of the driving force. These results are in line with what has been observed in different works in the literature, even using different test systems.

Finally, it is concluded that the use of underinhibited systems can really be an economically and technically interesting application, and can enable the realization of marginal projects. But, this evaluation must be done carefully, respecting the geometry, the types of fluids and the types of flow found in the production system.

As future works, we suggest to do similar studies in systems containing other kinds of hydrate inhibitors, as the LDHIs (low dosage hydrate inhibitors) and other fluids, in different flow conditions.

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Responsibility Notice

The authors are the only responsible for the paper content.

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