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HYDRATE PHASE EQUILIBRIUM USING WATER-BASED DRILLING FLUID

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Abstract. *In oil and gas pipelines, some issues like wax and asphaltene precipitation and hydrate formation are common and a source of concern in flow assurance. During drilling and production operation, the injection of thermodynamic inhibitors, such as sodium chloride (NaCl), is a traditional way to avoid hydrate formation. It is important to identify the conditions that hydrate formation occurs to prevent hydrate plugs during the exploration and production of oil. This study includes phase equilibrium measurements using a high pressure cell and the isochoric method with pure water, with and without NaCl, water-based drilling fluid and pure methane. The experimental data obtained were also compared with the thermodynamic model developed by the group. The experimental results indicated the effect of the salt inhibitor present in the water-based drilling fluid in the phase equilibrium. Also, the results obtained suggest others components of the drilling fluid have few or almost no influence on the hydrates prediction curve.*

Keywords: *gas hydrate, phase equilibria, drilling fluid*

1. INTRODUCTION

Gas hydrates are crystalline structures of water resembling ice. The crystals are formed by water molecules linked by hydrogen bonding and stabilized by gas molecules. Small molecules such as methane, ethane, propane, nitrogen and carbon dioxide are compounds that may stabilize gas hydrates. An ideal scenario for hydrate formation is the presence of water and gas at high pressures and low temperatures, conditions often observed during the exploration and production of oil and gas, particularly in offshore transport lines. Therefore, there is a growing interest in understanding this phenomenon, since severe offshore oil exploration conditions have been more frequent in latest years.

Among the problems associated with hydrate formation, one can emphasize the increased pressure drop in pipelines, productions losses and increased accident risks. Such operational challenges occur because hydrate crystals often agglomerate due to the attraction force (capillary effect). Two cases of interruption of the drilling process were reported by Barker e Gomez (1989). The cases presented by the authors occurred on the West Coast of the United States, where choke and kill lines were blocked and hydrates were detected in the Gulf of Mexico after a long stopping period.

The petroleum exploration industry adopts some strategies to avoid the hydrate formation by the use of thermodynamic inhibitor, for instance or by maintaining the hydrate in flowable conditions, which is accomplished by anti-agglomerant inhibition. Salt and alcohol are thermodynamic inhibitors that shift the equilibrium curve, requiring higher pressures and lower temperatures to form hydrates (Sloan and Koh, 2008). The disadvantage of using

thermodynamic inhibitors is the need for large amounts of inhibitors in the oil fields. The cost to the petroleum industry with methanol acting as hydrates formation inhibitor is around \$ 740,000/day. (Creek et al. 2011).

The risk of hydrate formation can be assessed through the collection of phase equilibrium curves. Several authors have conducted experimental studies to obtain phase equilibrium data using different methods, such as isochoric, isothermal, Raman spectrometry and calorimetry (Kakitani, 2014; Hu et al., 2017; Bishnoi and Dholabhai, 1993; Jager and Sloan, 2001 and Cha et al., 2016). There are also thermodynamic models to predict the hydrate equilibrium curve, based on the van der Waals and Plateeuw ideal solid theory or Gibbs energy minimization (Kakitani, 2014; Ballard e Sloan, 2002; Sloan e Koh, 2008).

In order to carry out the drilling activities of the oil wells with safety and maximum efficiency it is necessary to know the ideal conditions of operation, besides having a good control of the process. Experimental studies related to drilling fluid components as hydrate formation promoters were performed by Ebeltoft and Yousif (1997) and Cha et al. (1988). Therefore, it is important to know the performance of the components of the drilling fluid to predict hydrate formation conditions. This work presents an experimental procedure for studying the influence of the drilling fluids components in hydrates phase equilibria using methane gas. Also, experiments were performed with two other systems: pure water + methane gas and water + methane+ 10 wt% NaCl to compare with the experimental data of the drilling fluid. All the experimental results were compared with the thermodynamic model developed in our group (Kakitani, 2014).

2. EXPERIMENTAL PROCEDURE

Phase equilibrium measurements were performed for methane hydrates using two high pressure cells. Figure 1 illustrates the scheme of the experimental apparatus, whereas the main equipment is the phase equilibrium cell. The tests with drilling fluid sample were performed using two pressure cells with a maximum volume of 30 mL and 500 mL. Both cells have sapphire windows for viewing, enabling monitoring of the cell contents during the experiment. The cells were placed in a cooling jacket coupled to the temperature-controlled bath.

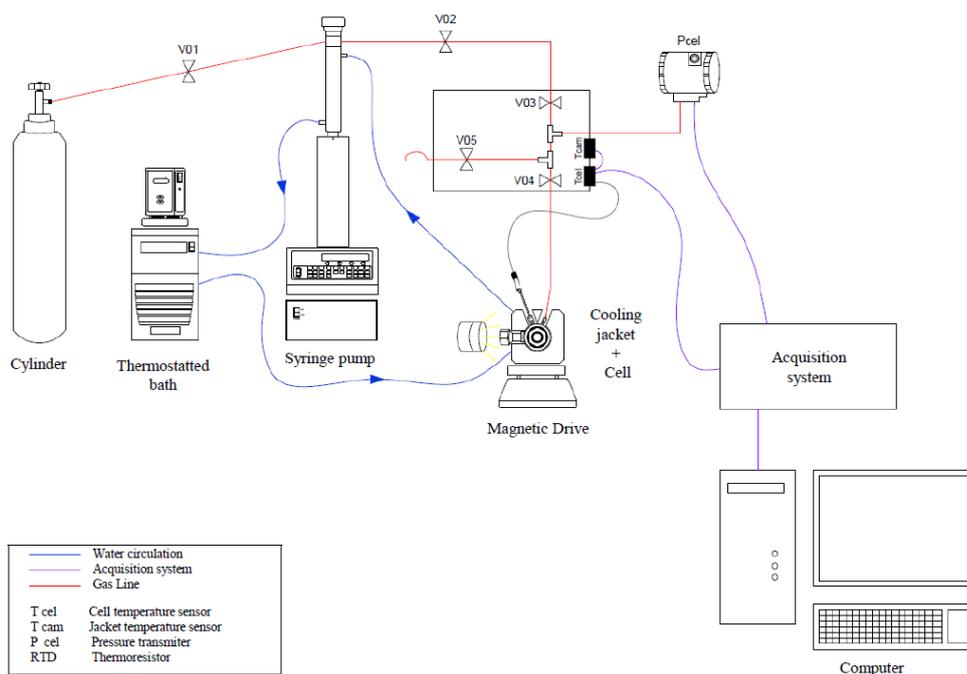


Figure 1. Scheme of experimental apparatus used for methane hydrate phase equilibrium measurements.

The experimental apparatus was composed by four parts: (1) gas system: responsible for pressurizing the cell; (red line in Figure 1), (2) temperature control: responsible for maintaining and changing the temperature (blue line in Figure 1), (3) pressure cell and (4) data acquisition: pressure and temperature data were recorded throughout the test. The materials used were pure methane and water based drilling fluid, in which water and the inhibitor salt sodium chloride are the most abundant components in the fluid. The drilling fluid used in the experiments was composed by water, sodium chloride, xanthan gum, HPA, sodium bicarbonate, magnesium oxide, calcite and polifoam and it was supplied

by Petrobras. The gas phase was used in the experiments was pure methane 4.5 (99.99995% purity) supplied by White Martins. For the tests with pure water+methane and water+methane+10wt%NaCl it was used distilled water and the NaCl was supplied by Petrobras.

The experiments were performed using the isochoric method and closed system. The first step in this procedure is the preparation of the system, which includes cleaning the cell, the injection of the components (liquid phase and gas phase) and checking for gas leakage. In order to remove the maximum amount of air from the cell, gas was purged three times before the final charge with gas to the predetermined pressure. For the leak test, the system is monitored for about 3 hours without any change in the conditions of temperature and pressure.

The experiment started at values of pressure and temperature above the expected equilibrium point. Then, the system was cooled down to induce the hydrate formation which is accompanied by a pressure drop resulting from the occlusion of gas molecules in the hydrates. The temperature of the system was increased to induce hydrate dissociation. The phase equilibrium point was the intersection between the cooling line and dissociation line. This procedure was used for obtaining the experimental data presented in the next section.

3. RESULTS AND DISCUSSION

A 10 mL sample of water-based drilling fluid (BR CARB SAPINHOA 11) and methane gas were used for the experimental tests. The operating pressure and temperature range in the experiments were, respectively, from 7 to 12 MPa and 278 to 284 K.

Figure 2 shows the result of an experimental cycle involving drilling fluid and methane gas. It is possible to identify each step of the experiment. Point 1 represents the start of the experiment. The line between points 1 and 2 represents the process of cooling the system to a temperature associated with hydrate formation. Then, the phenomenon of nucleation and growth of hydrate crystals takes place (line 2-3), where the evident pressure drop occurs due to the occlusion of the gas molecules in the crystalline structures formed by the water molecules. And finally, the gradual dissociation (process represented between points 3, 4 and 5) of the hydrates is performed until the break-even point (point 5) is reached and the hydrates are completely dissociated. From point 3 to 4 a rapid dissociation was carried out and from point 4 to 5 a slow dissociation was performed, ie, the temperature was increased at a rate of 0.1 °C per hour. Point 6 represents the end of the experiment where the initial pressure and temperature operating conditions are reached.

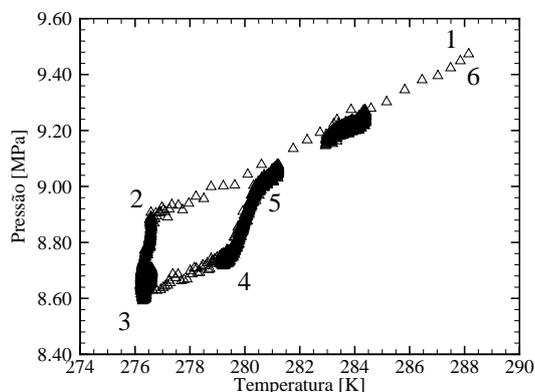


Figure 2. Pressure versus temperature graph for hydrate formation of drilling fluid + methane.

Through the front sapphire window of the 30 mL equilibrium cell it is possible to follow the phenomena that occur throughout the experiment. Figure 3a shows the beginning of the experiment (point 1 in Figure 2), where the gas phase and the liquid phase (drilling fluid) are present. Figure 3b shows the beginning of hydrate formation (point 2 in Figure 2). At this stage nucleation has already occurred and the hydrate is in the crystal growth phase. Figure 3c shows the beginning of dissociation (point 3 of Figure 2). In Figure 3d the system is observed along the dissociation (point 4 in Figure 2). When the experiment is finished, the system returns to the gas and liquid phase (similar to Figure 3a).

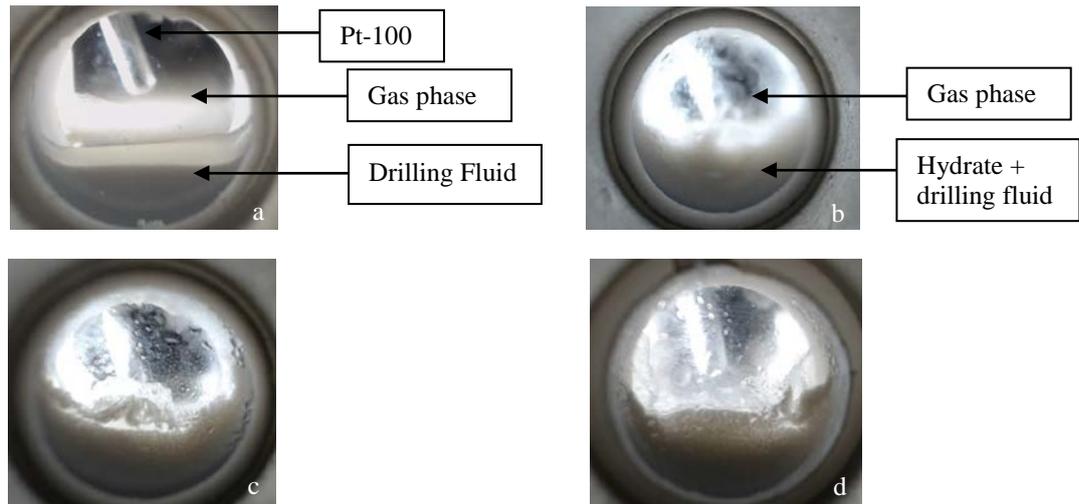


Figure 3. Sequence of images of the complete cycle of the phase equilibrium experiment of hydrates. a) Start of the experiment. b) Beginning of hydrate formation. c) Beginning of dissociation. d) Dissociation step.

For each initial, previously established, pressure and temperature conditions, a similar experiment to that represented in the Figure 2 was performed and as a consequence an equilibrium point of each cycle was obtained. The equilibrium point is obtained graphically by performing two linear regressions, one in the cooling line (straight between points 1 and 2) and one in the dissociation line (straight between points 4 and 5). The intersection of the lines gives the coordinates of the equilibrium point of this experiment.

The experiments with pure water + methane and water + methane + 10wt% NaCl were carried out in the 500 mL pressure cell and the volume of water inserted was 100 mL. The experimental procedure was similar to that performed with drilling fluid, however, the temperature increase in the slow dissociation step was 0.05 ° C per hour.

The results obtained with the drilling fluid + methane systems; pure water + methane and water + methane + 10% by mass of NaCl, Table 1, Table 2 and Table 3, respectively.

Figure 4 shows the phase equilibrium results of methane hydrate using drilling fluid and pure water and results from the model (Kakitani, 2014). The model was based on the equality of chemical potentials of all species in all the phases (liquid water, hydrate and vapor). The Soave Redlich-Kwong equation of state was employed for the phase equilibrium properties of the hydrocarbon fluid phase. The curve *a* is the hydrate phase equilibrium for pure water and the curve *b* is the hydrate phase equilibrium in the presence of salt inhibitor (10 weight% of NaCl). The square points in the curve *b* are results from the drilling fluid and the circle points are the results from water + methane + 10wt% NaCl system.

Table 1 Phase equilibria data of methane hydrates using drilling fluid.

Temperature (K)	Pressure (MPa)
279,33	7,84
279,41	7,97
279,48	7,64
280,91	9,09
283,15	11,76
284,02	11,76

Table 2 Phase equilibria data of methane using pure water.

Temperature (K)	Pressure (MPa)
278.84	4.53
279.84	4.98
280.03	4.99
281.41	5.96
282.32	6.56

Table 3 Phase equilibria data of methane hydrates using water + 10wt% NaCl.

Temperature (K)	Pressure (MPa)
276.97	5.74
278.10	6.45
278.14	6.58
279.28	7.43

According to Figure 4 the interference of the thermodynamic NaCl inhibitor (second component in higher concentration in the drilling fluid sample) can be observed by displacement of the equilibrium curve to the left. The results obtained with drilling fluid were compared with results obtained from a thermodynamic model with a water system, methane gas and 10wt% NaCl. The maximum deviation obtained between the experimental data of the drilling fluid and those of the model was 15.2%. It was observed that the influence of the other components of the drilling fluid is not significant, and the drilling fluid can be "analyzed" as a system (NaCl + methane + water).

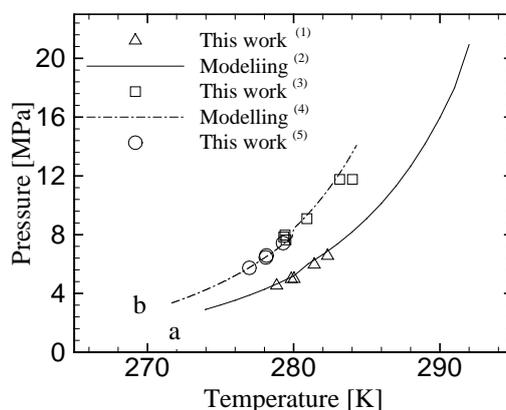


Figure 4. Comparison with the results from thermodynamic model and experimental data. (1) experimental data for water + methane system; (2) thermodynamic model results for water + methane system (Kakitani, 2014); (3) experimental data for the drilling fluid and methane system; (4) thermodynamic model results for water + methane +10 wt% NaCl system (Kakitani, 2014); (5) experimental data for water+methane+10wt% NaCl.

Comparing the drilling fluid data with water + NaCl system results, it is possible to notice the proximity of the experimental data and also the results follow the same tendency of the thermodynamic model curve (Kakitani, 2014), which simulate a system consisted of water + gas methane + 10wt% NaCl. The comparison of the results obtained with drilling fluid and the pure water + methane gas system proves the NaCl inhibition performance present in the drilling fluid composition.

4. CONCLUSIONS

The experimental results presented in this study indicated that the water-based drilling fluid presented the effect of the thermodynamic NaCl inhibitor on the hydrate formation. The results obtained suggest that the other components of the drilling fluid have little or no influence on the prediction of the hydrate equilibrium curve, that is, the factors influencing the hydrate phase equilibrium would be water, gas composition and presence of thermodynamic inhibitors. The similar behavior between the results obtained with the drilling fluid and the system with water + NaCl reinforces the assumption of the little influence of the other components of the drilling fluid in the hydrate phase equilibrium. Due to the diversity of components in the drilling fluids, preliminary studies with separate components of the drilling fluids would help to the understanding of the influence of each component on the hydrate formation.

5. ACKNOWLEDGEMENTS

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