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EXPERIMENTAL PHASE EQUILIBRIUM OF CARBON DIOXIDE HYDRATES WITH MEG ABOVE THE UPPER QUADRUPLE POINT

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Abstract. *Equilibrium curves for carbon dioxide hydrates have an upper quadruple point, which appears due to the condensation of carbon dioxide. Above this point, there is a scarcity of experimental data in the literature, especially with the presence of additives, such as monoethylene glycol (MEG). In order to better understand the behavior of the system in this region, an experimental procedure was developed to work with high pressures to obtain liquid water-hydrate-condensed carbon dioxide (L_W-H-L_{CO2}) equilibrium curves. The experimental three-phase equilibrium data was compared with those in the literature, showing consistent agreement. MEG was used as a thermodynamic inhibitor in the aqueous phase in order to evaluate its inhibition effect on the equilibrium of hydrates.*

Keywords: *hydrates, phase equilibrium, carbon dioxide, upper quadruple point, MEG.*

1. INTRODUCTION

Given certain thermodynamic conditions, molecules of water form caged like structures that can capture gas molecules in its interior, forming what it is known as gas hydrates. Hydrates characteristics is highly dependent on the type of gas being encapsulated by the caged like structure (e.g., carbon dioxide, methane, ethane, nitrogen, etc.) (Sloan and Koh, 2008).

Cage structures are usually relatively large and highly symmetrical, which depend on the type of molecule hosted in it. In addition, the molecules that make up the cage can be in an allotropic state, stabilized by the guest molecule (Powell, 1948).

In oil extraction industries, hydrates of natural gases when formed can block pipelines, causing damage and preventing normal operations. That way, it is important to know under what conditions do hydrates form and what effects certain additives have on its phase equilibrium. Thermodynamic inhibitors (e.g., alcohols, salts, etc.) can change the conditions in which hydrates form, preventing their appearance. Monoethylene glycol (MEG) is commonly used in oil industries to prevent the formation of hydrates by changing the equilibrium conditions (Sloan and Koh, 2011).

Carbon dioxide is considered a contaminant in natural gas. Its presence alters the properties of the hydrates formed. Hydrates of carbon dioxide are also denser than water, causing a decrease in volume when formed. Some oil fields can have up to 50% in CO_2 content, changing the phase equilibrium of the system (Sloan and Koh, 2011).

Hydrates of carbon dioxide have an upper quadruple point in its phase equilibrium that could be reached in oil extraction. This point is characterized for the presence of four phases: liquid CO_2 (L_{CO2}), vapor CO_2 (V_{CO2}), liquid water (L_W) and hydrate (H). CO_2 requires relatively high pressures to become a liquid, so that robust experimental apparatus are necessary to be able to determine equilibrium conditions above the Q_2 point (Sloan and Koh, 2008).

This work reports new data on CO_2 hydrates with and without MEG above the upper quadruple point in liquid water-hydrate-liquid carbon dioxide (Lw-H-L_{CO2}) phase equilibrium. The experimental data are compared with literature data on dissociation conditions of carbon dioxide hydrates in the presence of pure water to show the inhibiting effects of the thermodynamic inhibitor MEG in aqueous solutions.

2. METHODOLOGY

In order to determine the temperature of hydrate equilibrium for a specific pressure, an isobaric process is used. Similar to Besnard (1991), the volume of added or removed guest compound, which is necessary to maintain a constant pressure, is used to determine the variation of volume of the components present inside the equilibrium cell. By measuring

the volume change with temperature, maintaining constant pressure, it is possible to determine the equilibrium conditions graphically.

2.1 Experimental apparatus

The equilibrium cell apparatus used is the same one described previously by Ferrari et al. (2016) and Guembaroski et al. (2016), shown in Fig. 1. The equilibrium cell (illustrated in Fig. 2) is made of stainless steel and can operate with a maximum pressure of 30 MPa with a temperature control ranging from 233 to 473 K.

The pressure of the cell is maintained constant with a syringe pump that adds or removes liquid CO_2 as necessary. The pressure within the cell is measured with a pressure transducer (S-11 WIKA), which has a range from 0 to 40 MPa, with an uncertainty of 0.30% (95% confidence interval).

The temperature is controlled by programing the circulating bath to the desired temperature ramp, which pumps fluid trough the circulating jacket of the cell. A thermocouple (PT100) measures the temperature inside the cell, having a range from 223.15 to 623.15 K with an uncertainty of 0.17 K (95% confidence interval). A magnetic stirrer bar was also used to provide better mixing of the phases.

The sapphire windows are used to light and visualize the interior of the cell, making it possible to confirm the presence of hydrates with the digital camera ((9) in Fig. 1).

The aqueous solutions of MEG were prepared gravimetrically using an accurate analytical balance with an accuracy of 0.1 mg.

2.2 Materials

Carbon dioxide was provided by White Martins Industrial Gases. MEG was provided by Vetec Fine Chemicals. Table 1 shows the purities and chemical information of these compounds. Distilled water was used and prepared in our own lab.

Table 1. Materials used in the hydrate equilibrium study.

N.	Chemical Name	Symbol	Purity	Chemical Structure
1	Carbon Dioxide	CO_2	99.9995 mass%	O=C=O
2	Monoethylene Glycol	MEG	99.5 mass%	HO OH

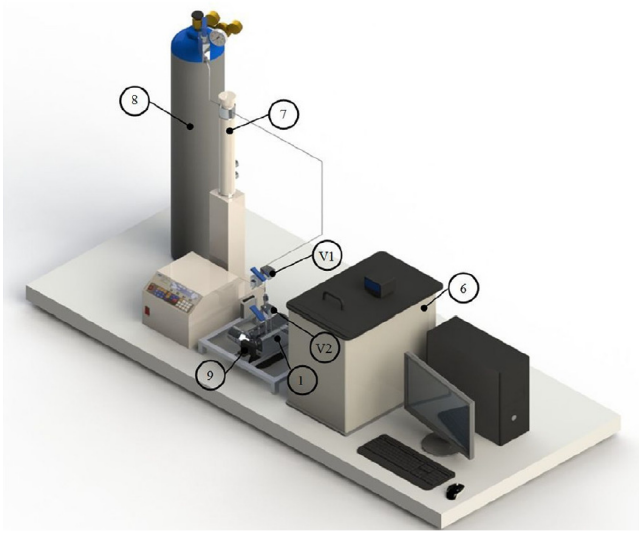


Figure 1. Phase equilibria experimental apparatus. Key components: (1) equilibrium cell, (6) thermostatic bath, (7) syringe pump, (8) carbon dioxide cilinder, (9) digital camera (Ferrari et al., 2016).

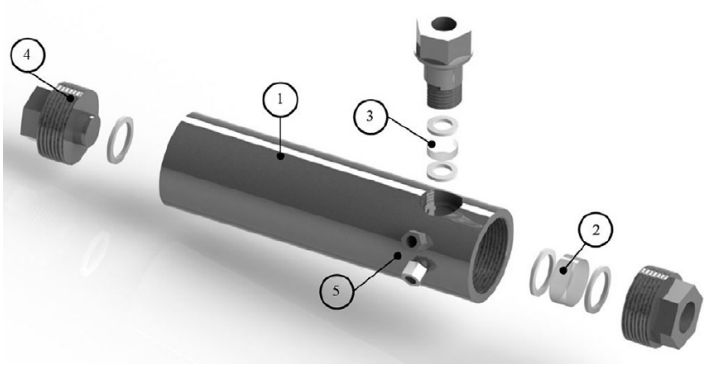


Figure 2. Equilibrium cell. Key components: (1) equilibrium cell, (2) and (3) sapphire windows, (4) back plug, (5) temperature, pressure and valve ports (Ferrari et al., 2016).

2.3 Isobaric experimental procedure

A known amount of distilled water is added to the cell at ambient pressure and temperature. If desired, a known amount of thermodynamic inhibitor is added to the water in this step. Next, a vacuum pump is connected to the system to remove air that is within the cell, inside the pipes and dissolved in the water. This procedure is carried out in order to increase the amount of CO_2 that can be mixed within the water phase.

The syringe pump is loaded with CO_2 and pressurized, being maintained at a constant temperature independently of the cell. Valve V2 is then opened, allowing CO_2 to enter in the cell. This is done at a certain pressure that allows for the visualization of three phases in the cell: vapor CO_2, liquid CO_2 and water ((a) in Fig. 3). Next, the syringe pump is set to the desired pressure, which is one high enough to make sure that the region we are working on is above the upper quadruple point (Liquid CO_2 – Liquid H_2O). This is confirmed by the presence of liquid CO_2 in the system ((b) in Fig. 3).

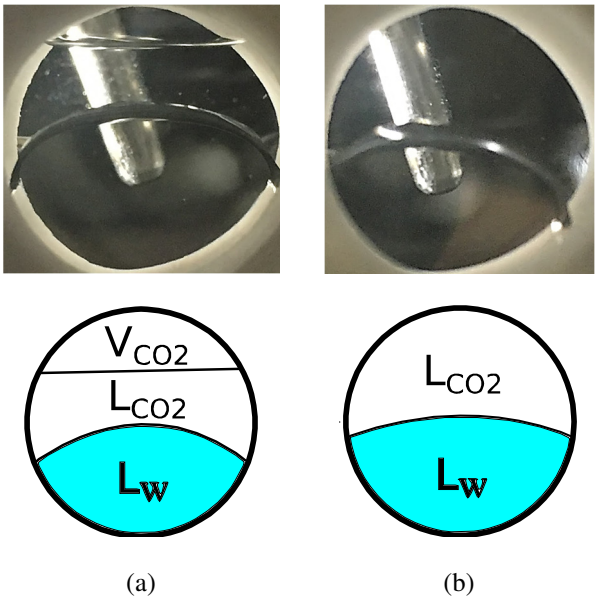


Figure 3. a) charging of the cell with carbon dioxide (L-L-V), b) pressurized system (L-L).

The temperature of the circulating bath is programed to decrease at a constant rate. This is done in order to obtain the cooling curve (illustrated as 1) in Fig. 4). Initially, the volume decreases linearly due to the cooling of the system. When hydrates form, the volume decreases abruptly due to the transfer of molecules from the liquid phases to the solid phase (H). The point in wich hydrates form in the colling process variates as this is a stocastic process.

After hydrates are formed, the volume continues to decrease (curve 2) in Fig. 4) with temperature as now the system has liquid carbon dioxide and hydrates. Then, the cell is maintained at a temperature of 1 ºC for at least five hours in order to allow the maximum possible ammount of hydrates to form and prevent the formation of ice.

Next, the cell is slowly heated (curve 3) in Fig. 4) in order to reach the equilibrium point of hydrate dissociation. As the temperature of the cell contents increases, the volume increases initially mainly due to the expansion of the liquid phase. When hydrates start to dissociate, the volume rapidly increases with temperature. This is due to the release of

carbon dioxide and water molecules from the hydrate phase. After all hydrate has been dissociated, the volume start to increase just as it did when it was initialy being cooled.

The equilibrium point for the formation of hydrates is determined by the crossing of the cooling curve (1) in Fig. 4) and the hydrate dissociation curve (4) in Fig. 4). This procedure is known as the isobaric method (Sloan and Koh, 2008).

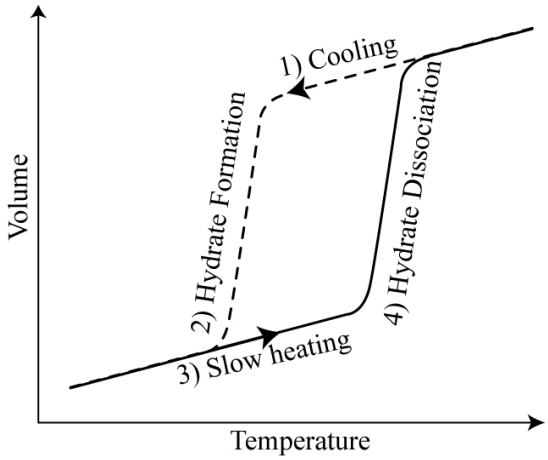
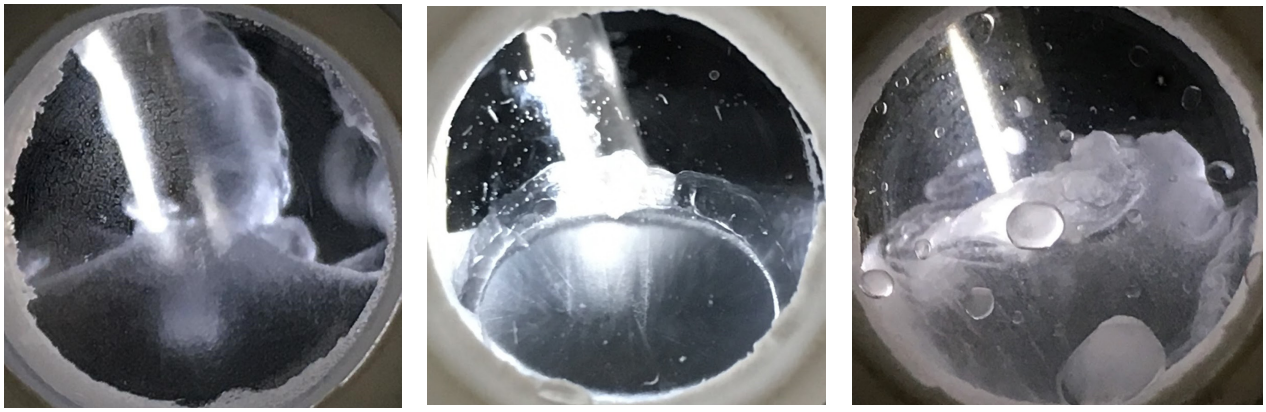


Figure 4. Isobaric procedure for determing the equilibrium conditions for formation of hydrates.

Figure 5 shows hydrates formed in some of the experiments done. All of the experiments were done above 0 °C in order to make sure that the solid phase was made of hydrates and not ice. That can also be confirmed by the decrease in volume, which is due to the formation of a more dense solid phase. If ice was formed, the opposite would have been observed.



P = 8.5 MPa P = 13 MPa P = 15 MPa

Figure 5. Hydrates formed at different pressures for systems with CO_2 and pure water.

3. RESULTS AND DISCUSSION

In order to validate the experimental procedure, several points were taken for the equilibrium formation of carbon dioxide hydrates with pure water. Each of these points were repeated four times and the result is the average.

Figure 6 shows a typical data graph obtained for the developed isobaric process. As expected, it is possible to obtain the cooling line and cross it with the dissociation line. At the start of the slow heating step, a decrease of volume can be observed. This indicates that more hydrates are being formed. Since the mesured volume goes back to the values of the cooling line at the end of the dissociation, we can conclude that all the hydrates that have been formed were dissociated, resulting in the equilibrium temperature.

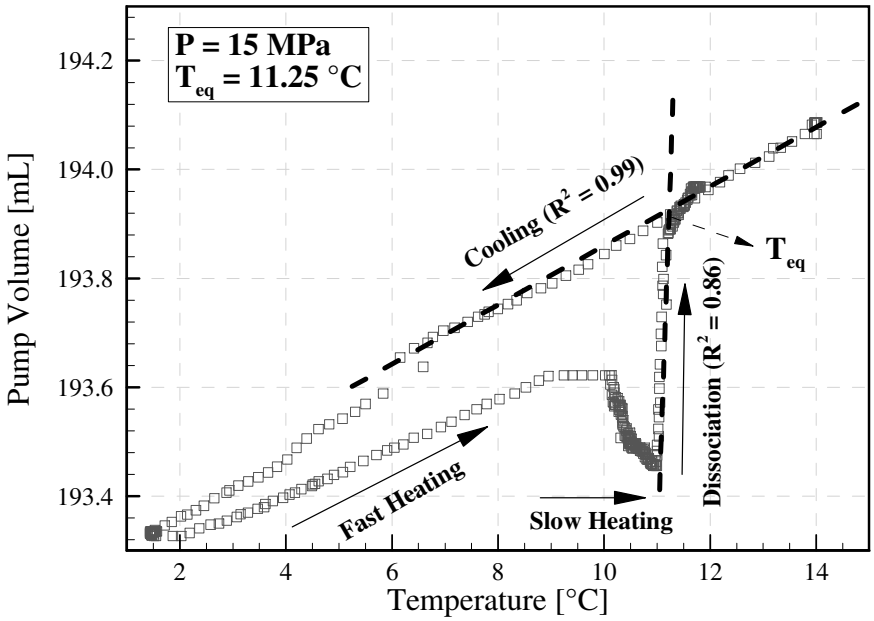


Figure 6. Typical graph obtained in the developed isobaric process.

During the procedure, the variation in volume with temperature can be evaluated in order to better understand the formation and dissociation process. Figure 7 shows how the volume decreases at the start of the procedure, with the cooling of the cell. During the period of constant temperature, a sudden rise in temperature (a) is observed due to the formation of hydrates, which is an exothermic process. In addition, when hydrates form, it is possible to identify a decrease in volume due to the transfer of CO_2 molecules from a less dense phase (L_{CO2}) to a denser one (H). The cooling line will then be from the start of the experiment (time zero in Fig. 7) until the point just before the hydrates formed ((a) in Fig. 7).

Next, a fast heating is promoted until a temperature close to the start of dissociation. Finally, the slow heating step is started with consequent dissociation of hydrates, which can be verified by the rise in volume ((b) in Fig. 7). This increase of volume is due to the transfer of molecules from the solid phase (H) to the two liquid phases. The dissociation line will be between the two changes in the inclination of the volume curve, observed at (b) in Fig. 7.

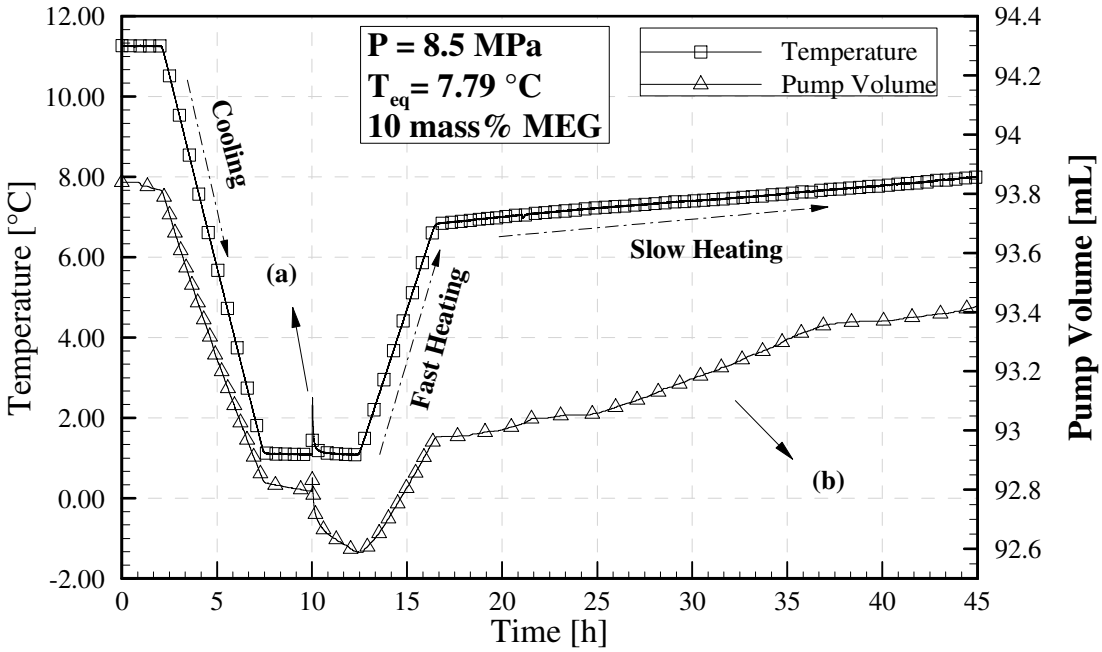


Figure 7. Behavior of measured volume with temperature of the cell. (a) Formation of hydrates; (b) Dissociation.

The comparison with experimental data is shown is Fig. 8. CSMGem (Sloan and Koh, 2008) was also used to create prediction curves for the formation of hydrates in regions above and below the upper quadruple point. In Fig. 8, the upper

quadruple point is characterized by being the intersection of the hydrate equilibrium curve with the liquid carbon dioxide equilibrium curve.

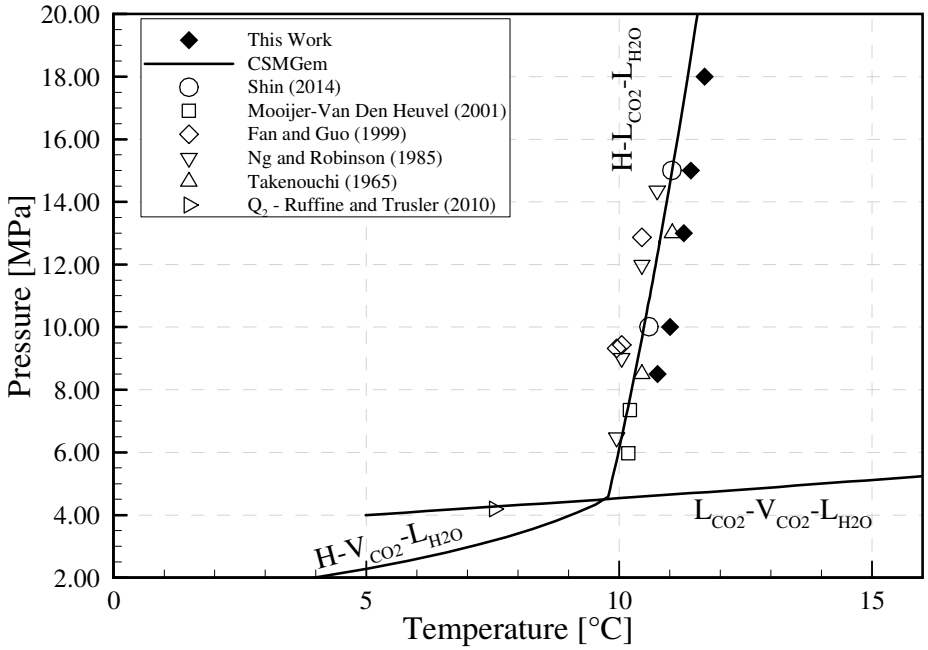


Figure 8. Comparison of the present work results for CO_2 and water only with CSMGem and available data.

A thermodynamic inhibitor, MEG, was used to evaluate its effect on the formation of carbon dioxide hydrates. Above the upper quadruple point, there is very little data with the addition of thermodynamic inhibitors. That way, data collected in this work was not previously available in literature.

Figure 9 shows the results obtained for mass percentages of 10% and 20% of MEG. This data is then compared with predictions from the CSMGem software, represented with continues lines, and the Hu-Lee-Sum correlation for inhibited systems, represented with dashed lines.

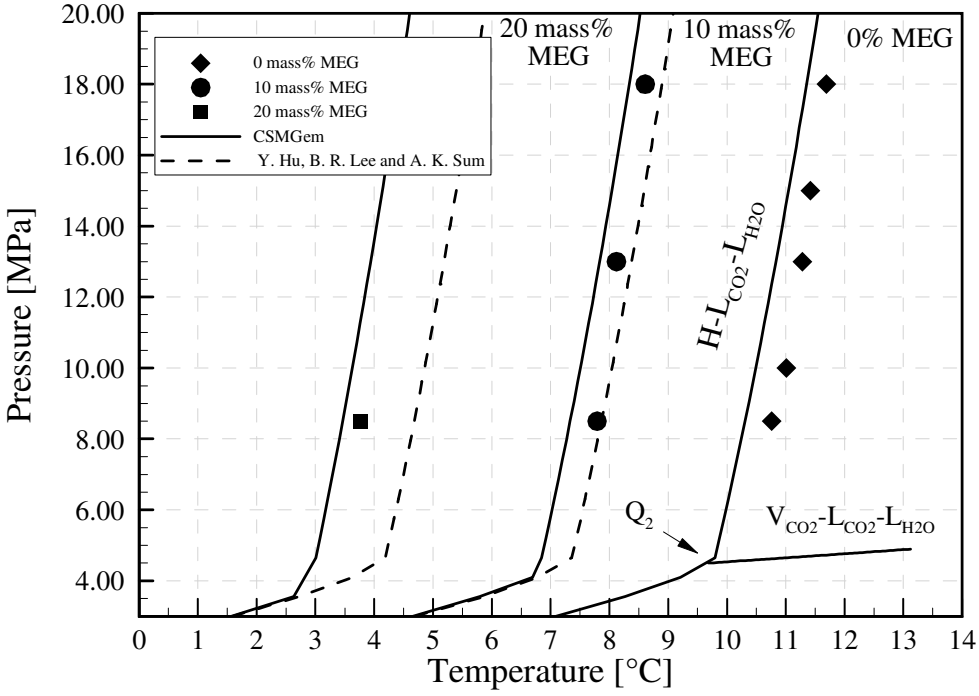


Figure 9. Data obtained in this work with the addition of MEG and comparison with CSMGem and the correlation for inhibited systems developed by Y. Hu, B. R. Lee and A. K. Sum (2017).

3.1 Linearity with the Clausius-Clapeyron relation

The Clausius-Clapeyron equation allows for checking the consistency of the data collected. By plotting the natural logarithm of pressure by the inverse of temperature, a linear relation is expected for reliable data. Figure 10 shows that the data collected for hydrates of CO_2 and pure water has a very good linearity ($R^2 = 0.99$) and similar inclination when compared to available data. Similarly, Fig. 11 shows the linearity for 0% and 10% mass percentages of MEG.

$$ln(P) = -\frac{\Delta H_{Dissociation}}{zR}\left(\frac{1}{T}\right) \tag{1}$$

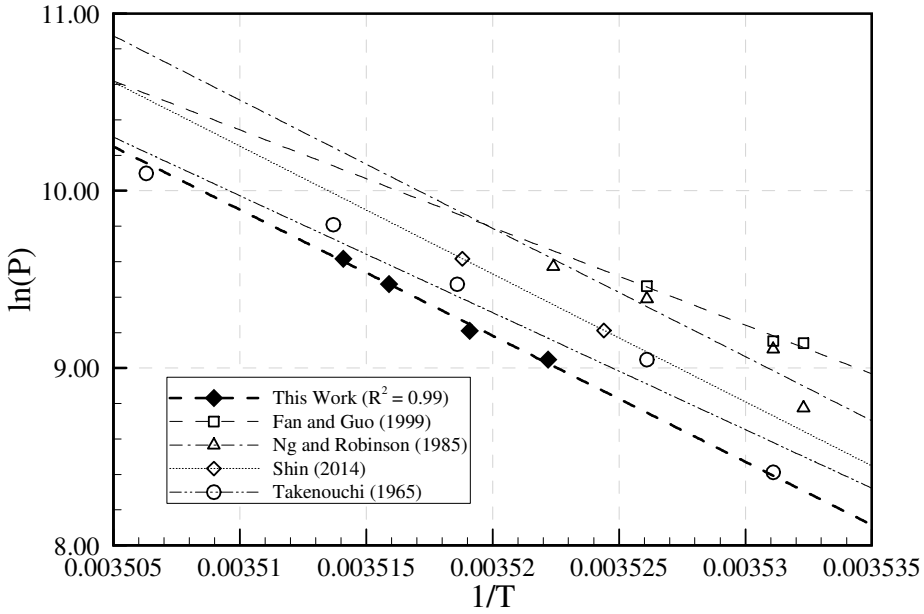


Figure 10. Linearity of the Clausius-Clapeyron equation for hydrates of CO_2 and pure water.

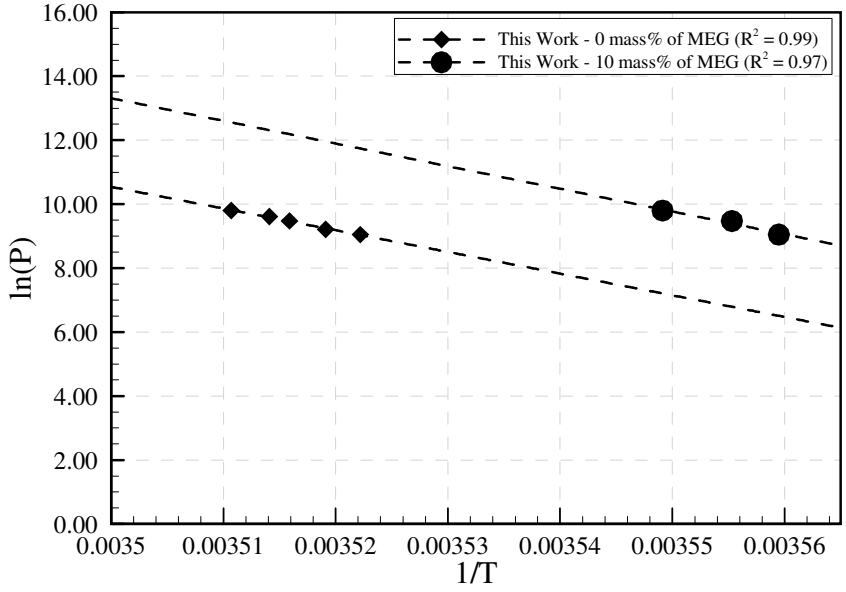


Figure 11. Fitting for Clausius-Clapeyron relation for carbon dioxide hydrates with and without MEG.

4. CONCLUSIONS

Equilibrium curves for the formation of carbon dioxide hydrates with and without MEG above the upper quadruple point were experimentally measured.

To evaluate the influence of a thermodynamic inhibitor, mono ethylene glycol (MEG) was used with mass concentrations of 10% and 20% in aqueous solution. As expected, the addition of this chemical compound was able to decrease the equilibrium temperature for the formation of hydrates by a significant amount. In addition, the higher concentration of MEG caused a higher decrease in the equilibrium temperature.

The results obtained were fitted with the Clausius-Clapeyron relation with a very good linearity, showing that the data collected is consistent with what was expected from the relation. For the results that were taken with pure water and CO_2, inclinations were very similar to available data.

5. ACKNOWLEDGEMENTS

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