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EXPERIMENTAL PHASE EQUILIBRIUM OF CO_2 HYDRATES ABOVE Q_2 INHIBITED WITH MEG, NACL AND ISOPROPANOL

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Abstract

Gas hydrates are crystalline solids formed from the union of water cages and gas guest molecules. As formed, gas hydrates can be a flowing solid phase or agglomerate and being an interruption or blockage in pipelines, causing damages and preventing normal flow. The motivation of this study arises from the lack of data in the literature that explores both conditions of high pressures and concentrations of carbon dioxide. The purpose of this work is the experimental study of the phase equilibrium of carbon dioxide hydrates with the presence of thermodynamic inhibitors, specifically above the upper quadruple point (Q_2). The thermodynamic inhibitors used were monoethylene glycol (MEG), isopropyl alcohol, and sodium chloride (NaCl). Two distinct experimental methodologies were developed in this study to achieve high enough pressures to allow the condensation of the gas phase. The pressures were evaluated between 10 and 26 MPa. Two different thermodynamic inhibitors were performed: MEG and isopropyl alcohol in concentrations between 2-30%wt, after NaCl in concentrations of 5 and 10%wt as well as their mixtures were experimentally determined. The results were also compared with the NUEMHyd, an in-house software for the hydrate formation prediction developed by Sirino et al. (2018) which uses the Cubic-Plus-Association EoS.

Keywords: hydrates, carbon dioxide, NaCl, MEG, isopropanol, upper quadruple point.

1. INTRODUCTION

In some scenarios of oil industries, where production is associated with the massive presence of gas, as well as with critical pressure and temperature conditions, some compounds know as gas hydrates or technically called “clathrate hydrates” may arise and constitute an impasse in the production sector. These compounds are similar to ice, that through hydrogen bonding, water molecules link together to form a cavity that encapsulates gas molecules of a second type (a low molecular weight), forming a solid phase. Characterized by the presence of free cavities, which allows the allocation of these hosted molecules, the structures of these materials are currently known by sI, sII, and sH types, but the most common are those of the sI and sII type (Zerpa et al. 2011). A visual representation of the described structures, as well as the gases that generate them, are shown in Fig. 1 below.

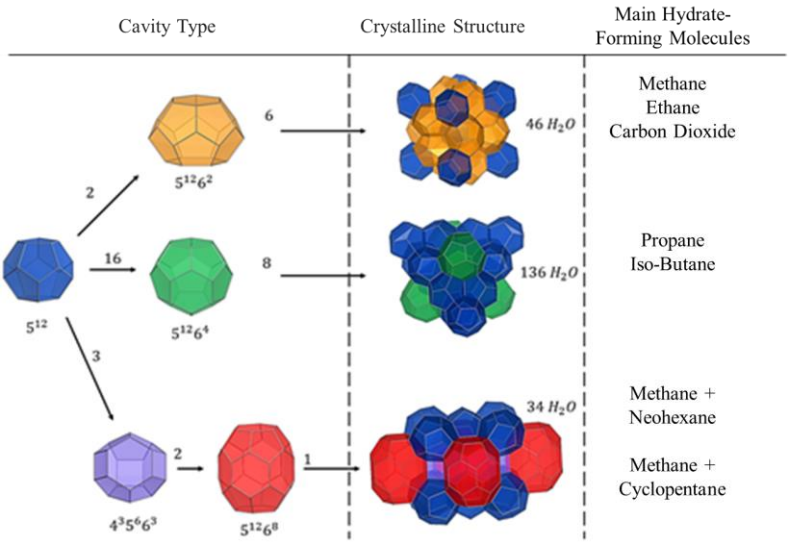

Figure 1 - Detailed visual representation of gas hydrate structures
Available from: Adapted from (Sirino et al. 2018)

Such hydrate compounds can also be found naturally in the permafrost of arctic regions, where natural gas is trapped inside the solid hydrate phase. This brings a potential asset to be explored in the industry. Other potential applications include the possibility of storing natural gas in form of hydrates, which may facilitate transport, as it would be in a solid-state, making it even safer and compact. In addition, hydrates can be found in our daily lives in the form of carbohydrates, and liquid hydrates, and also used in separation processes, such as in the treatment of effluent gases, where the formation of hydrates capture gases, and in the desalinization of seawater (Obanijesu et al. 2011).

After their formation, and their possible agglomeration, a new non-flowing solid phase is created, and in gas and oil industries they can trigger blockages (Fig. 2) in pipelines, causing damages and preventing normal operations. It is a flow assurance problem, where their occurrences can have high economic costs. The characterization of the hydrate phase equilibrium is of significant importance to predict if and when such solid-state structures form.

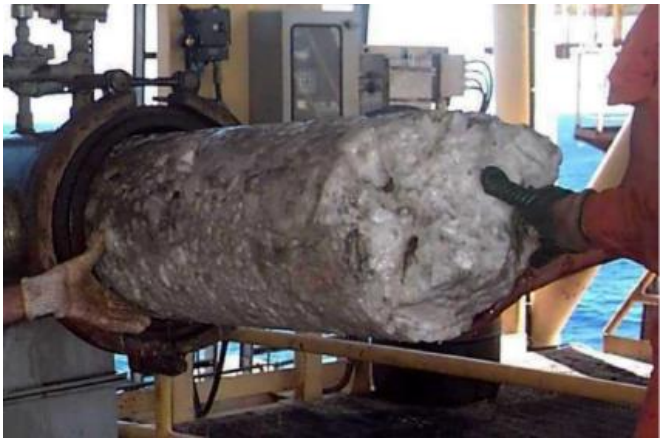

Figure 2 - Hydrate plug being removed from a pipeline in a Petrobras installation.
Available from: (Zerpa et al. 2011)

In some regions as in the pre-salt reservoirs, like in the Brazilian southeast coast, the carbon dioxide can be found as a natural contaminant in petroleum, and make part of produced gas composition, reaching up concentrations between 8% and 12% while other can have concentrations above 50% in relation the other present components in natural gas (Melo et al. 2011). The Fig. 3 shows the phase equilibrium of the H_2O - CO_2 system. The equilibrium curve where vapor CO_2 forms hydrates (L_W-H-V) is widely studied with a higher quantity of experimental data available in

the literature. However, the curve where liquid CO_2 forms hydrates (L_W-H-L_{CO2}) is less studied, even though it is a frequently encountered situation, where carbon dioxide presents itself under conditions of high pressure and relatively low temperatures

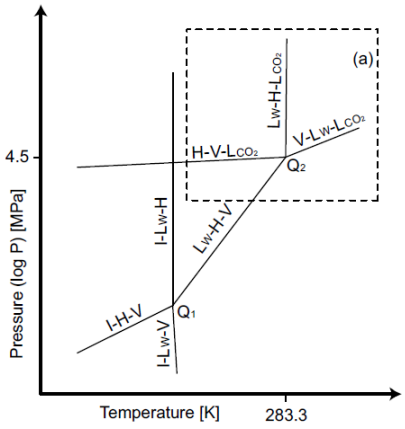

Figure 3 - Phase equilibrium of the H_2O/CO_2 system – Emphasis on quadruple point region
Available from: Adapted from (Sloan, 2008)

In the region above the Q_2 point, CO_2 molecules from the liquid phase are trapped to form the hydrate solid phase, differently from the region below Q_2, where gas molecules diffuse from the gas phase to the solid hydrate phase.

To prevent the formation of these compounds, or to allow their formation in a controlled manner, thermodynamic inhibitors can be used, shifting the hydrate formation equilibrium region to a safe operational condition. Among the most common inhibitors, alcohols and glycols, like ethanol and MEG are widely used. But, other thermodynamic inhibitors, less usual, like the isopropyl alcohol, have been used to due in workover/simulations scenarios, as well as diluting agents of H_2S scavengers or antifouling.

The focus of this work is on evaluating the formation of hydrates in this region, obtaining experimental data for conditions in which condensed carbon dioxide combines with water to form hydrates in the presence of the aforementioned thermodynamic inhibitors. This characterization was developed in two different methodologies, isobaric and isochoric procedure, using MEG, sodium chloride, and isopropyl alcohol as thermodynamic inhibitors. Besides, all results were submitted to a comparison with the NUEMHyd, a robust prediction model developed by Sirino et al. (2018), which uses Cubic-Plus-Association (CPA) as an equation of state (EoS).

2. METHODOLOGY

2.1. Experimental approach

Measurements of phase behavior at high pressures are usually complex and difficult to achieve. There are several types of experimental devices for investigating phase equilibrium in high pressures, each with its advantages and disadvantages, in which what will prevail will be the objective for which the data is intended.

The experimental procedure presented here was developed to allow the formation of hydrates above the upper quadruple point (Q_2), where pressures are high enough to allow the vapor CO_2 to condense. For such development, an equilibrium cell made of stainless steel that can operate with pressures of up to 30 MPa was used for the laboratory tests. The temperature in this system is controlled through a heat exchanger, with a programmable circulating bath. The bath has a temperature control ranging from 233 K to 473 K. The cell has the possibility of a direct connection to a direct supply system or is directly connected to a syringe pump, which can add or remove CO_2 as necessary. The syringe pump is kept at a constant temperature with water running through its cooling jacket and a circulating bath. A probe (PT-100) measures the temperature inside the cell, which has a range from 223.15 K to 623.15 K and an uncertainty of 0.21 K (95% confidence interval). A pressure transducer also measures the pressure inside the cell, which has a range from 0 to 40 MPa and uncertainty of 0.30% (95% confidence interval). The signals are received by a computer, which records the data over time.

The equilibrium cell can be used in two configurations: visualization and high-pressure. For the visualization configuration (Fig. 4a), two sapphire windows allow for the lighting and direct visualization of the interior of the cell. This allows for the visual confirmation of the formation of hydrates or the condensate phase. To prevent problems with leakages at high pressures, the sapphire windows can be replaced with stainless steel blind plugs. The high-pressure

configuration (Fig. 4b) allows for maximum tightening of the cell plugs, preventing leakages without the risk of breaking the sapphire window. A magnetic stirrer is used for agitation to provide better mixing of the compounds.

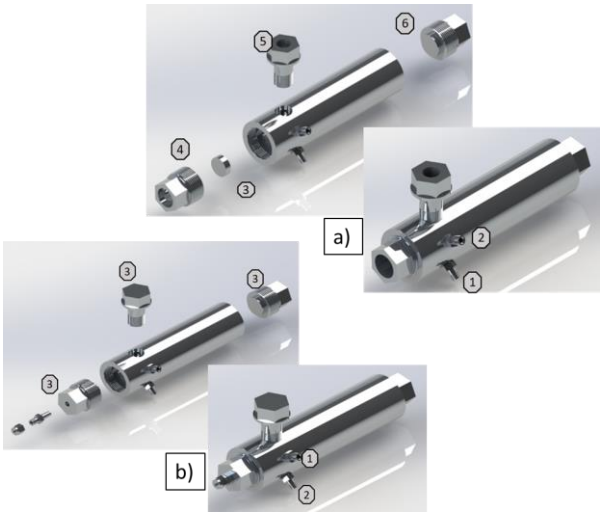

Figure 4 – Equilibrium cell a) Visualization conformation, (1) Pressure and load connections, (2) temperature measurement, (3) sapphire window, (4) front plug, (5) lighting window and (6) rear plug. b) High-pressure configuration, (1) pressure and loading connections, (2) temperature measurement, (3) plugs.

The confirmation of the formation of hydrates can be done in two ways: visually and graphically. As they form, carbon dioxide molecules are transferred from the liquid phase to the solid hydrate phase. Initially, a known amount of water is added to the equilibrium cell at ambient temperature and pressure. For experiments done with thermodynamic inhibitors, they are added to the water-rich phase in this step.

After the cell is properly prepared, the cooling process is initiated. To make sure that the equilibrium is maintained at each data point, this step is performed at a rate of 2 K per hour. When cooling, the volume initially decreases due to the thermal contraction of the liquid phases. With lower temperatures, the density increases, causing a decrease in volume/pressure. When hydrates form, a sharper decrease in volume/pressure is expected. The graphical determination of the equilibrium point can be done either by crossing the cooling and dissociation lines or directly finding the change in inclination after the dissociation is completed (shown as T_{eq} in Fig. 5 a) and b)).

The experimental procedures are known as the isobaric and isochoric search method. After the temperature of the system goes lower than the equilibrium temperature, hydrates may form. However, hydrate formation is a stochastic process, with a region where the system is in a metastable state, as shown in Fig. 5. In other words, it is in thermodynamic conditions for hydrates to be formed but they may not for kinetic reasons. Therefore, the equilibrium temperature for the formation of hydrates can be defined as the temperature at which all hydrates are dissociated, which will always be the same for a given system (Sloan, 2008).

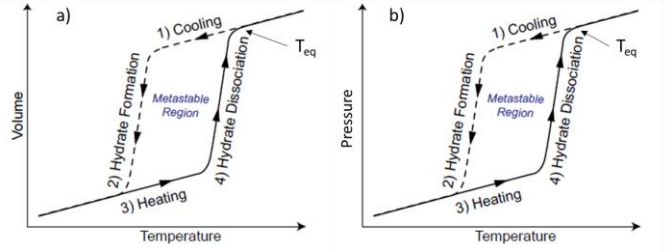

Figure 5 - Steps in the experimental procedure: (a) Isobaric cooling and formation of hydrates; (b) Isochoric cooling and formation of hydrates
Available from: Adapted from (Sloan, 2008)

2.2. Numerical approach

The phase equilibrium model implemented in this work, known as NUEMHyd, is an in-house software for the hydrate formation prediction developed by Sirino (Sirino et al. 2018). It is based on the isofugacity concept. The fugacity of each component in the non-hydrate phases has been calculated by the CPA-EoS (Kontogeorgis et al. 1999). The hydrate phase has been modeled using the ideal solid solution model developed by van der Waals and Platteeuw.

The CPA-EoS combines a cubic EoS, initially the Soave-Redlich-Kwong (SRK), with an association term derived from the Wertheim's theory, which is similar to the used in the Statistical Association Fluid Theory (SAFT). In terms of pressure, the CPA-EoS can be expressed for mixtures as:

$$P = \frac{RT}{v_m - b} - \frac{a}{v_m\left(v_m + b\right)} - \frac{1}{2}\frac{RT}{v_m}\left(1 + \frac{1}{v_m}\frac{\partial \ln\left(g\right)}{\partial\left(1/v_m\right)}\right)\sum_i x_i \sum_{A_i}\left(1 - X_{A_i}\right) \tag{1}$$

where R is the universal constant of the gases, v_m is the molar volume, b is the SRK co-volume parameter, a is the SRK temperature-dependent energy parameter, g is the radial distribution function, A_i denotes the bonding site A of component i, X_{Ai} is the fraction of A-sites of the molecule i that are not bonded with other active sites, and x_i is the mole fraction of component i.

In the right-hand side of the Eq. (1), the first two terms are identical to the SRK EoS and describe the fluid as free particles with a weak attraction between them, these terms are responsible for the physical part of the CPA EoS. The third term in the right-hand side of the Eq. (1) is the association contribution of the CPA, which depends on the association strength between hydrogen bond-forming molecules. As presented in the work of Chapman et al.,1990 the association term is derived from Wertheim's first-order thermodynamic perturbation theory (TPT-1), and it is assumed that the activity of each bonding site is independent of the others bonding sites on the same molecule. Besides, steric hindrance and cooperativity effects are regarded. For non-associating substances, the association term is equal to zero and the CPA EoS reduces to the SRK.

The key element of the association part is the X_{Ai}, i.e. the fraction of molecules not bonded at site A. The calculation of this fraction depends on the association scheme that is going to be adopted in the model and it must be consistent with the geometry and the distribution of charges of the involved molecules. Table 1 shows some associative parameters of pure fluids. This scheme exhibits the number and type of association sites in each molecule. According to the terminology of Huang and Radosz (Huang and Radosz, 1990) in this work, it has been adopted the 4C-scheme (two protons donors + two protons acceptors) for water and MEG, and the 2B-scheme (one proton donor + one proton acceptor) for the isopropyl alcohol. The carbon dioxide was modeled as a non-self-associating compound that is capable of cross-associate with self-associating compounds (i.e. water, alcohols, glycols), this type of interaction is known as solvation. The carbon dioxide was modeled with two electrons acceptors sites.

The model also uses the Kihara potential and extended the equations developed by van der Waals and Platteeuw to calculate phase equilibrium for single and mixed gas hydrates. Their approach allowed the hydrate formation pressures and temperatures to be determined by equating the chemical potential of water in all phases. It has been applied effectively to calculate phase behavior of hydrates, both simple and complex, in that way of avoiding the introduction of empirical parameters.

Table 1 – CPA parameters for pure fluids.
Available froms: (Kontogeorgis et al. 1999) and (Tsivintzelis et al. 2011)

Fluid	Association Scheme	a_0 (L^2 bar/mol^2)	b (L/mol)	c_1	ε (bar L/mol)	β
H_2O	4C	1.2277	0.0145	0.6736	166.55	0.0692
CH_3OH	2B	4.0531	0.0310	0.4310	245.91	0.0161
CH_3O_8H	2B	1.058161	0.2487	0.30615	248.87	0.0105303
C_2H_5OH	2B	8.6716	0.0491	0.7369	215.32	0.0080
$C_2H_6O_2$	4C	10.8190	0.0514	0.6744	197.52	0.0141
CH_4	n.a.	2.3204	0.0291	0.4472	-	-
C_2H_6	n.a.	5.5093	0.0429	0.5846	-	-
C_3H_8	n.a.	9.1539	0.0587	0.6672	-	-
C_4H_{10}	n.a.	12.9094	0.0747	0.7021	-	-
CO_2	n.a.	3.5079	0.0272	0.7602	-	-
H_2S	3B	3.8605	0.0292	0.5022	54.40	0.0583
N_2	n.a.	1.3733	0.0260	0.4984	-	-

3. RESULTS AND DISCUSSION

MEG, Isopropyl alcohol, and NaCl were evaluated as thermodynamic inhibitors in the formation of CO_2 hydrates. As discussed, they act by interacting with water molecules, making them less available to form hydrates, thus it is expected that their presence will cause a decrease in the equilibrium temperature for the same pressure. In Table 2, the grid test of both procedures is presented alongside some results, predictions of software products, and models.

Table 2 – Grid Tests

Isochoric Procedure		**Isobaric Procedure**	
Pressure(MPa)	**10.0;17.0;21.0;26.0**	**Pressure(MPa)**	**8.5;13.0;18.0;25.0**
Non inhibited system	Pure Water	Non inhibited system	Pure Water
2-PrOH (% wt)	2;5;10;25	MEG (% wt)	10;20;30
NaCl (%wt)	5;10	NaCl (%wt)	5;10
2-PrOH (% wt) + NaCl (5%wt)	5;10;25	MEG (% wt) + NaCl (5%wt)	10;20;30

First of all, the isobaric procedure was performed in order to compare the experimental data of the pure (uninhibited) system with the inhibited data with the different concentrations to evaluate the inhibition effect of MEG, mass concentrations of 10%, 20%, and 30% were used initially. Fig. 6. a) shows the data obtained for the equilibrium point of carbon dioxide hydrates inhibited with MEG. It is plotted as pressure versus temperature at the equilibrium for the pressures of 8.5, 13.0, 18.0, and 25.0 MPa. The concentrations are in the mass percentage of the aqueous phase. As expected, MEG acted as a thermodynamic inhibitor, decreasing the equilibrium temperature for the formation of hydrates. Also, a higher concentration caused a higher inhibition effect.

Figure 6 b) shows the results obtained for hydrates of CO_2 inhibited with sodium chloride. Concentrations are in mass percentages in the aqueous phase. Similarly to MEG, NaCl acts as a thermodynamic inhibitor, lowering the equilibrium conditions for the formations of hydrates. Additionally, a higher concentration of salt resulted in a higher inhibition effect, acting as a thermodynamic inhibitor.

To evaluate the influence of the water salinity, a fixed amount of 5 mass% of NaCl was used with different concentrations of MEG. This way, it is expected that a lower concentration of MEG would be necessary for achieving the same inhibition effect when compared with a pure water system. Fig. 6, c) shows the results from this work for the system with 5% of NaCl and different concentrations of MEG.

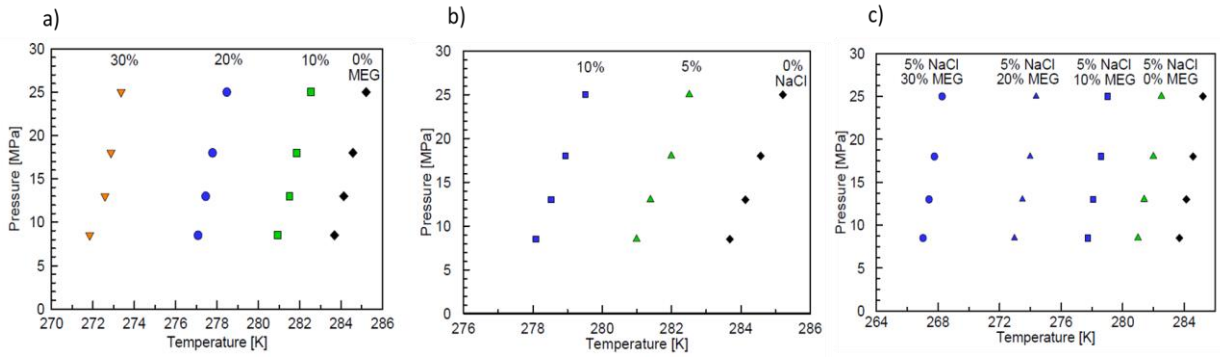

Figure 6 – Results of isobaric experimental procedure: (a) equilibrium point of carbon dioxide hydrates inhibited with MEG;(b) for hydrates of CO2 inhibited with sodium chloride; (c) system with 5% of NaCl and different concentrations of MEG.
Available from: Adapted from (Cordeiro, 2019)

Furthermore, the results of this procedure were then compared with the model for inhibited systems from Sirino et. al. (2018) model (indicated as red continuous lines) and some correlations and software, visually arranged in Fig. 7 below. The results returned a good agreement concerning that predicted by the model in question and relation to the other correlations.

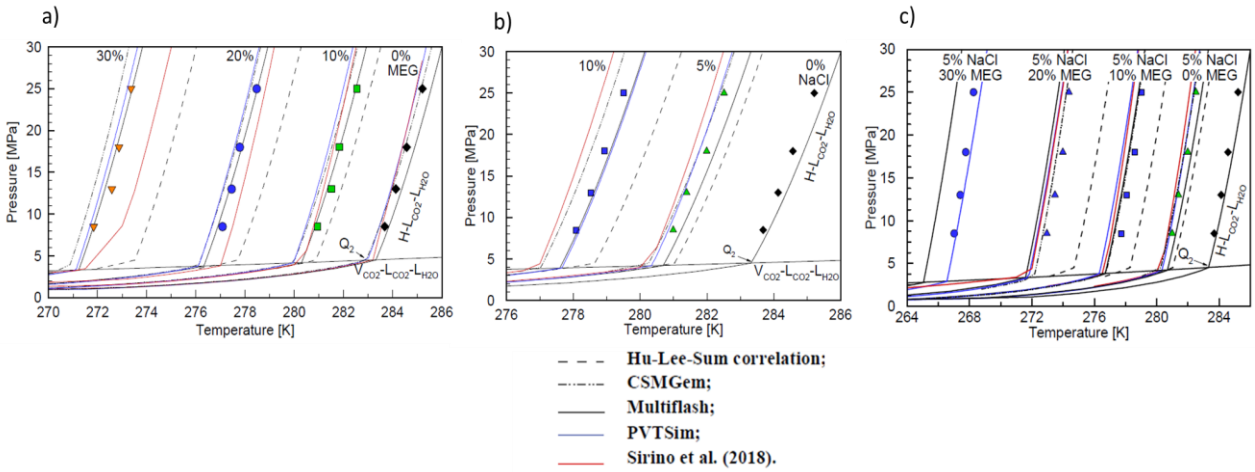

Figure 7 – Comparison of the isobaric experimental procedure with software and correlations: (a) equilibrium point of carbon dioxide hydrates inhibited with MEG;(b) for hydrates of CO2 inhibited with sodium chloride; (c) system with 5% of NaCl and different concentrations of MEG.
Available from: Adapted from (Cordeiro et al. 2019)

In sequence, for the isochoric procedure, in order to compare the experimental data of the pure (uninhibited) system with the inhibited data with the different concentrations to evaluate the inhibition effect of isopropyl alcohol, mass concentrations of 2%, 5%, 10%, and 25% were used initially. Fig. 8, a) shows the data obtained for the equilibrium point of carbon dioxide hydrates inhibited with 2-PrOH. It is plotted as pressure versus temperature at the equilibrium for the pressures of 10.0, 17.0, 21.0, and 26 MPa. The concentrations are in the mass percentage of the aqueous phase. As expected, 2-PrOH acted as a thermodynamic inhibitor, decreasing the equilibrium temperature for the formation of hydrates.

Figure 8, b) shows the results obtained for hydrates of CO_2 inhibited with sodium chloride. Concentrations are in mass percentages in the aqueous phase. Similarly to 2-PrOH, NaCl acts as a thermodynamic inhibitor, lowering the equilibrium conditions for the formations of hydrates. Additionally, a higher concentration of salt resulted in a higher inhibition effect, acting as a thermodynamic inhibitor.

As known, the water produced in offshore oil extraction is naturally inhibited due to the presence of salts. To evaluate the influence of the water salinity, a fixed amount of 5 mass% of NaCl was used with different concentrations of 2-PrOH. This way, it is expected that a lower concentration of 2-PrOH would be necessary for achieving the same inhibition effect when compared with a pure water system. Fig. 8, c) shows the results from this work for the system with 5% of NaCl and different concentrations of 2-PrOH. The concentrations are in mass% in the aqueous phase.

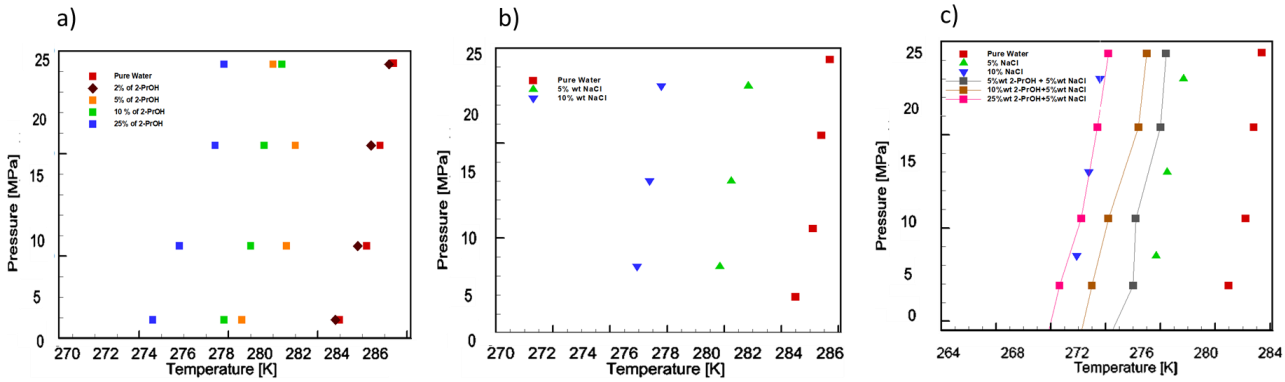

Figure 8 – Isochoric experimental procedure: (a) equilibrium point of carbon dioxide hydrates inhibited with 2-PrOH;(b) for hydrates of CO_2 inhibited with sodium chloride; (c) system with 5% of NaCl and different concentrations of 2-PrOH.

Likewise, for the data obtained, using the numerical model for inhibited systems from Sirino et. al. (2018)(Sirino et al. 2018) mentioned above, the results of this procedure (isochoric) were then compared with, and also with other commercial software like multiflash and PVTsim, visually arranged in Fig. 9 below. It is worth noting that the correlation data for the experiments where NaCL is the inhibitor or is part of the inhibition system, its prediction and implementation is still under development, so, in Fig. 9, de results are shown partially only to 2-PrOH.

The results returned a good agreement about that predicted by the model in concentration up 10% or inhibitor, losing the thermodynamics sense in low concentrations scenarios, with the model developed by. To the other software, the results showed a good agreement. The model ended up behaving unexpectedly at lower concentrations, due to a possible and apparent change in structure where 2-PrOH, incites the change from the sI structure to the sII structure

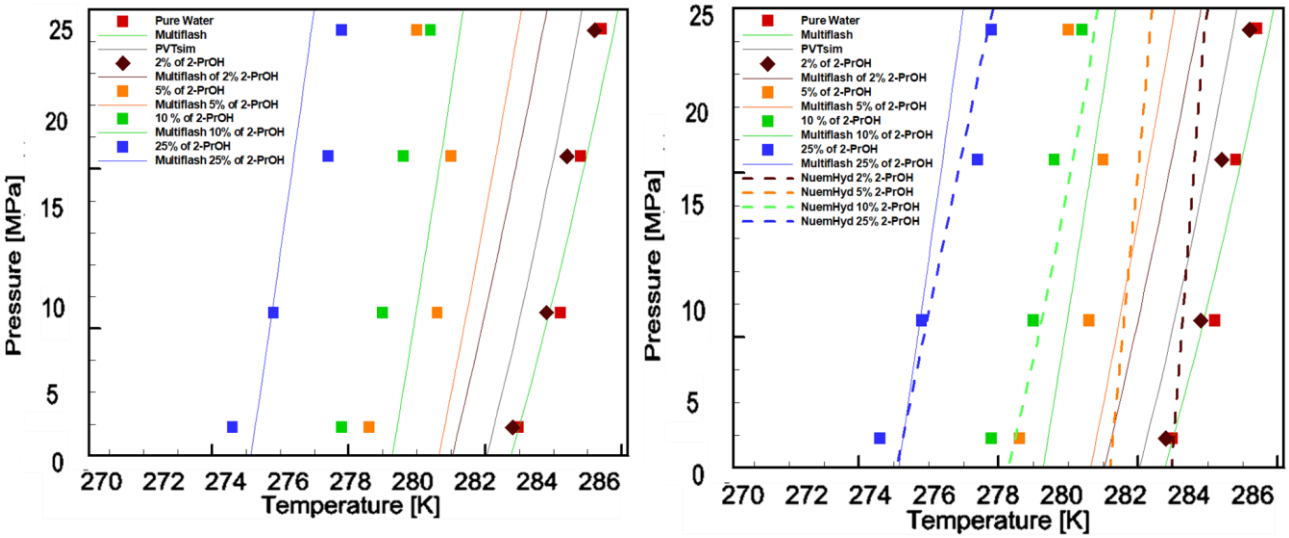

Figure 9 – Comparison of the isochoric experimental procedure with software and correlations: (a) equilibrium point of carbon dioxide hydrates inhibited with the 2-PrOH comparison with Multiflash; (b)) the equilibrium point of carbon dioxide hydrates inhibited with the 2-PrOH comparison with the model developed by (Sirino et al. 2018).

The results of the optimization of the parameters of the state equation that models the hydrate characterization system are still in the development phase, so a small disparity in the preliminary results can be observed.

4. CONCLUSIONS

An isobaric and an isochoric experimental procedure was performed to achieve high enough pressure to allow the condensation of the gas phase. Experimental data for the equilibrium conditions of CO_2 hydrates were obtained. The pure water system data was used to validate the experimental procedure by comparing the results with the model developed. To evaluate the inhibition effect of thermodynamic inhibitors, MEG, 2-PrOH, and NaCl different concentrations were used, so the amount of thermodynamic inhibitor can be optimized in each situation. This way, the equilibrium conditions for CO_2 hydrates inhibited with pure and mixtures of NaCl and MEG and NaCl and 2-PrOH was determined.

Also in this study, a flash algorithm was implemented for equilibrium calculation in systems with clathrate hydrates, including the presence of thermodynamic inhibitor, and their mixtures (alcohols, salts, glycols). The model consists of a statistical thermodynamic approach for the hydrate phase based on the van der Waals and Platteeuw theory and the Cubic Plus Association (CPA) equation of state (EoS) for the fluid phases. In general, the developed algorithm provided results which are in good agreement with the experimental data performed and in multicomponent systems in the presence of mixtures of inhibitors. The reliability of the experimental data was evaluated for all the data collected in this work by comparison with this in-house software (NuemHyd), based on the model developed by Sirino et al. (2018).

Concerning inhibition, the MEG showed greater inhibition efficiency of gas hydrates, when compared to the inhibition power effect of isopropanol in liquid hydrate systems (above the upper quadruple point- Q_2). These results were already expected since isopropyl alcohol is not a usual inhibitor, about MEG, in oil and gas exploration scenarios. But its use in other lines like, in dedicated lines, and umbilical's and gas lift operations, where it can continue as a second inhibiting or diluting agent.

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