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EXPERIMENTAL PHASE EQUILIBRIUM OF CO_2 AND CH_4 HYDRATES INHIBITED BY ISOPROPANOL AND MIXTURES

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Abstract. *Under certain thermodynamic conditions, water molecules can combine with low molecular weight molecules to form crystalline structures known as hydrates. Blocking pipes due to the hydrates formation is a major concern in ensuring flow in the oil and gas industries. The motivation of this study arises from the lack of data in the literature that explores the isopropanol in conditions of a thermodynamic inhibitor or promoter, depending of the formation gas. In the present work, new experimental data for the phase equilibrium of inhibited carbon dioxide and methane hydrates were obtained for pressures between 20 and 260 bar, under concentrations ranging from 1 to 25%, in mass, of isopropanol and concentrations of 5 and 10%, in mass, of NaCl, in a high-pressure cell, using the isochoric method of experimental characterization. A thermodynamic model, previously developed, was applied and validated with the hydrate equilibrium conditions. This model uses the Cubic Plus Assosiation (CPA) state equation, for the fluid phases and a statistical approach, based on the Van der Waals-Platteeuw Theory, for the hydrated phase. Isopropanol was characterized as an inhibitor of CO_2 hydrates and a promoter of CH_4 hydrates, collaborating in the structural transition from the sI to the sII type.*

Keywords: *hydrates, carbon dioxide, methane, NaCl, isopropanol, CPA, upper quadruple point.*

1. INTRODUCTION

Gas hydrates are crystalline solids composed of water and a low molecular weight gas, formed under conditions of low temperature and/or high pressure. These compounds consist of water molecules interconnected through hydrogen bonds, forming a crystal structure with free cavities, which allow the allocation of light hydrocarbon molecules, coming from natural gas or liquid hydrocarbons (guest molecules) (SLOAN et al., 2011), as illustrated in Figure 1.

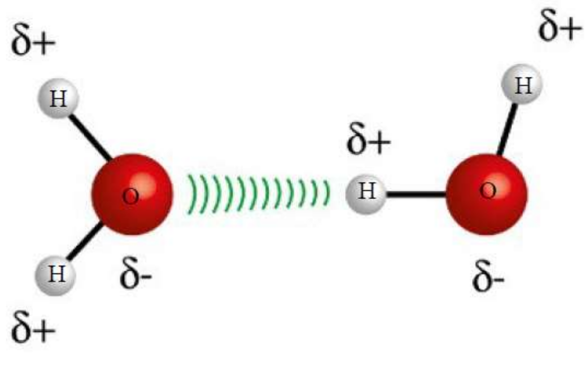

Figure 1 – Schematic representation of a hydrogen bond between two water molecules
Source: Adapted from (DIAS, 2019)

Characterized by 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).

The interaction between the host network (crystalline network formed by water) and the moleculehost occurs through van der Waals forces, with no chemical bond between them (SERVIO and ENGLEZOS, 2001). For a more usual designation, they are also known as gas hydrates or simply hydrates (HAMMERSCHMIDT, 1934). It is new structure is technically called clathrate hydrate. Commonly, developed studies analyze the occlusion of gas molecules such as methane, ethane, propane and carbon dioxide and, in some scenarios, their respective mixtures (SLOAN and KOH, 2008).

The formation of hydrate plugs can occur in industrial activities (Figure 2), causing inconveniences, such as blocking gas and oil transport lines. 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 may arise and constitute an impasse in the production sector. Research involving hydrates have been increasingly motivated mainly due to problems in exploration, in underexplored regions, such as the North Sea, Siberia, and in oil production or natural gas in deep waters, in the pre-salt layer.

Figure 2 – Illustration of a hydrate plug in a pipe
Source: TecPetro (2015)

In this scenario, it is necessary to characterize the equilibrium of hydrate phases in the oil and gas industry, in the regarding the flow guarantee. A frequently used method to prevent the formation of hydrates is the addition of thermodynamic inhibitors. These compounds act by changing the equilibrium conditions in that hydrates form. By adding a sufficient amount of inhibitor to a given system, the hydrate forming region can be shifted to a safe operating condition, where training may not occur or take place in a controlled manner.

Compounds such as isopropanol, MEG, ethanol and methanol act by changing the activity of water (via hydrogen bonding with the H2O molecules, Figure 3), thus altering the equilibrium of the hydrated phase for a safe operating condition. The amount of inhibitor needed can be optimized with the support of forecasting software and, mainly, from reliable experimental equilibrium data (SLOAN and KOH, 2008).

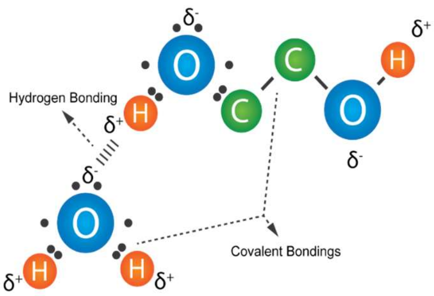

Figure 3 – Actuation of the thermodynamic inhibitor in a hydrated system
Source: Adapted from Cordeiro (2019)

In oil exploration and production, isopropanol is also a by-product often used during stimulation and workover, to aid rapid recovery of injected fluids and, in recent years, it has been found to be used in the prevention and correction of problems related to hydrates in offshore operations (KEENEY and FROST, 1975). Currently, the isopropanol is seen as a hydrate inhibitor, alongside other alcohols and glycols. However, this view is based purely on assumptions, due to lack of data in the literature. Lee et al. (2014) reported that, at low concentrations (between 1 to 10% by mass), isopropanol does not have no effect or little significant effect as a thermodynamic inhibitor or promoter, but in high concentrations (above 10% by mass), it probably acts as an inhibitor thermodynamic of CO_2 hydrates. One of the problems faced by the oil and gas industry in recent years is the formation of hydrates in umbilical. In scenarios where oil production takes place in greater depths (as in pre-salt), where the pipes are longer than the standards off-shore, in which these are required to adjust to the relief of the region, umbilical have emerged as a practical way of transporting chemical products to the bottom of the well or along the production line, in strategic locations and opportune times, as can be seen in the Figure 4.

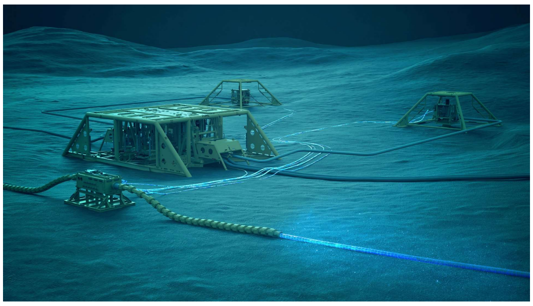

Figure 4 – Representation of (umbilical) chemical transport lines (off-shore)
Source: (Petrobrás, 2019)

This work aims to develop an experimental study of the phase equilibrium of CH_4 and CO_2 hydrates in pure and inhibited systems. The experiments were carried out with variations in the concentration of thermodynamics inhibitors (isopropanol and NaCl), as well as their combination, under conditions of pressures between 20 and 260 bar, in the presence of two types of gas (CO_2 and CH4), so that the respective points of equilibrium are found. A thermodynamic model previously developed by Sirino *et al.* (2018), the NUEMhyd, was applied and implemented with the hydrate equilibrium conditions obtained experimentally. This model uses the equation Cubic Plus Assosiation (CPA) for fluid phases and a statistical approach, based on the van der Waals-Platteeuw theory for the hydrated phase. Experimental data obtained were used to perform parameter optimizations of binary interactions, thus as parameters of kihara, given the scarcity of data in the literature.

2. METHODOLOGY

The experimental apparatus used is located in the Guarantee of Flow Laboratory, which is part of the Multiphase Flow Center (NUEM) of the University Federal Technology of Paraná (UTFPR). Figure 3.1 shows a simplified layout of the experimental bench and the equilibrium cell.

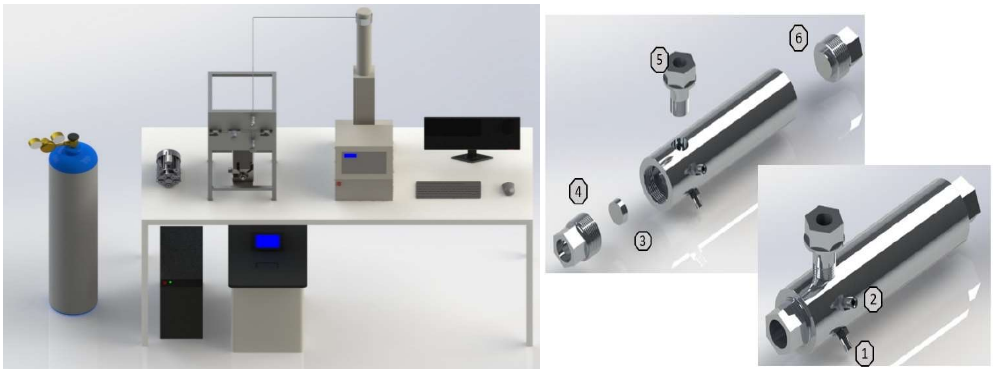

Figure 5 – Work bench / Equilibrium Cell - (1) Pressure and charge connections, (2) temperature measurement, (3) sapphire window, (4) front plug, (5) lighting window and (6) rear plug

2.1. Experimental Methodology

The isochoric method used in this work was the isochoric procedure. In this method, the volume remains constant as the temperature is gradually reduced, until the appearance of the first particles of hydrate. After the formation of hydrates, the temperature is gradually increased, always waiting for the thermodynamic equilibrium to be reached, until complete hydrate dissociation. The equilibrium point is obtained through the intersection between the cooling and dissociation curves. This is the most used technique for systems under high pressure (SLOAN AND KOH, 2008) Figure 6 shows the behavior of phases in typical characterization experiments.

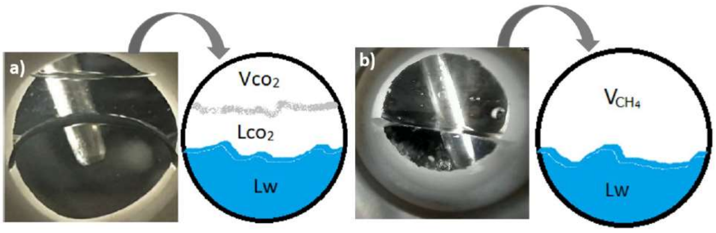

Figure 6 – Arrangement of phases. (a) CO_2, (b) CH_4.

2.2. Thermodynamics modelling

In thermodynamics, an equation of state is a mathematical relationship between the thermodynamic quantities of state, among state functions of a thermodynamic system. More specifically, an equation of state is a thermodynamic equation that describes the state of matter under a given set of physical conditions. It is a constitutive equation to which provides a mathematical relationship between two or more state functions associated with the matter, such as its temperature, pressure, volume, internal energy or entropy (Perrot and Pierre, 1998). State Equations are useful in describing the properties of fluids, mixtures of fluids or solids. In this work, their main use is to calculate the fugacity of phases in equilibrium with the hydrate phase, by the CPA.

Species that form hydrogen bonds generally exhibit behavior unusual thermodynamic. These interactions can strongly affect the properties of fluids and should be considered when designing a reliable thermodynamic model.

CPA applies uniquely to components present in hydrates and thermodynamic inhibitor systems, mainly because of their employment in the oil and gas industry. CPA is a mixed state equation as it combines the cubic equation of SRK with theories of association between molecules. It is important to note that for compounds not associative, the CPA reduces again to SRK. It has the following form given by Eq. 1:

$$P=\frac{RT}{v-B}+\frac{A}{v(v+B)}-\frac{1}{2}\frac{RT}{v}\left(1+\rho\frac{\partial \ln(g)}{\partial \rho}\right)\sum_i x_i \sum_{A_i}\left(1-X_{A_i}\right) \tag{1}$$

In the present work, the isopropanol component was implemented together with the model of Sirino *et al.,* (2018) (NUEMhyd), in association with the other gases already present in the thermodynamic modeling. The experimental data obtained in this work were used to validate the thermodynamic model developed by Sirino et al. (2018), which through the CPA equation of state, together with the van der Waals and Platteeuw model, is able to predict phase equilibrium.

For comparison purposes, the commercial MultiFlash® software was used. It also uses CPA as an equation of state.

3. RESULTS

To determine the equilibrium conditions of the hydrates of carbon dioxide and methane, initially without the presence of inhibitors, experiments were carried out through the static-synthetic methodology, isochoric procedure, in an equilibrium cell. In next, experiments were carried out with the presence of a thermodynamic inhibitor.

Different concentrations were selected in order to investigate the displacement effect of the phase equilibrium curve, that is, the hydrate inhibition or promotion potential. The inhibitors used in the tests were isopropanol, sodium chloride and a mixture of these.

3.1. Non inhibited systems

Section 3.1 provides a validation of the experimental methodology used through the obtaining equilibrium data for uninhibited systems. Looking for to validate the experimental methodology used, they were carried out initially the experiments with uninhibited systems, in order to obtain the behavior of the pattern of gas hydrates under study, validating existing literature data. The behaviors of both gas hydrates will be displayed and analyzed. A Comparison between the commercial software MultFlash™, and the in-house software, NUEMhyd was performed and the results can be seen in Figure 7 (A and B) below.

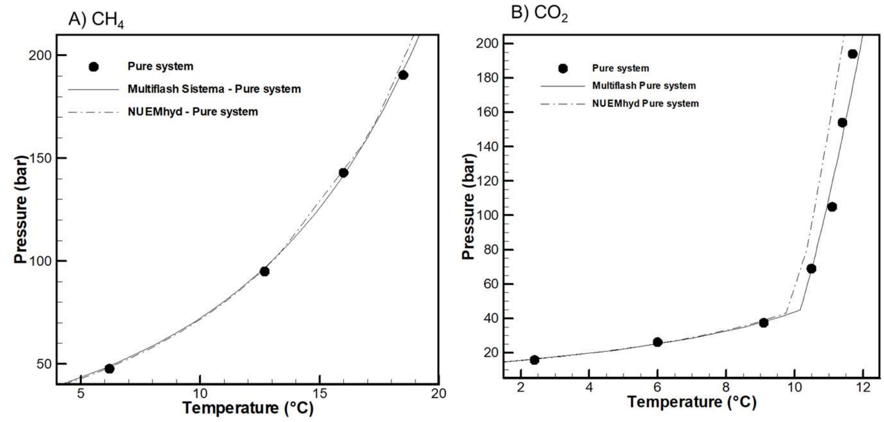

Figure 7 –Comparison with the softwares- (a) CH_4, (b) CO_2.

The software returned a good agreement, where the mean absolute deviations between the experimental data and NUEMhyd were 0.18% and 3.01% for CH_4 and CO_2, respectively. It is worth mentioning that for high pressure data, especially above the upper quadruple point, the NUEMhyd displays the largest deviations from the experimental data. This happens because of the Kihara parameters for CO_2 have been optimized only for the L_w-H-V region.

3.2. Inhibited systems: isopropanol as inhibitor and in mixtures - CO_2 hydrates

For all systems presented, isopropanol behaved as an inhibitor thermodynamic for high pressures (Q_2), and as a spectator or as an inhibitor of power lower inhibition at low pressures when compared to other usual inhibitors. Yours greater efficacy as a thermodynamic inhibitor was more evident in regions of higher pressures (Figure 8 – A and B).

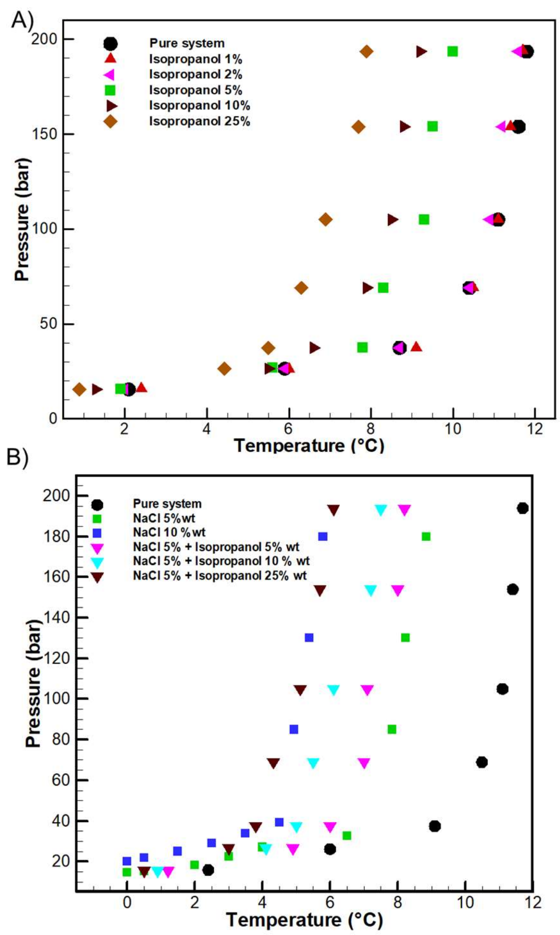

Figure 8 – (a)Isopropanol in mass concentrations 1-25%
(b) Isopropanol in mixtures systems(With sodium chloride) : ■ = Guembaroski (2016) and Cordeiro(2019).; ● = Present work (pure system); ▼= mixture of inhibitors

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It is observed that a higher concentration of isopropanol caused a greater effect of inhibition. It is possible to observe that the mixture reached a greater inhibiting power when compared to the inhibited systems isolated. The mixture data shifted to the left of it, reaching the concentration isolated from 10% NaCl, when 25% isopropanol is present by mass.

3.3. Inhibited systems: isopropanol as inhibitor and in mixtures – CH_4 hydrates

For the methane hydrate equilibrium data, the results raised discussions about the influence of isopropanol in the formation and promotion of gas hydrates, being conflicting in some situations (points as an effect of promotion/inhibition, possibility of occlusion and structural transition).

Isopropanol proved to be a thermodynamic promoter of methane hydrates for the investigated pressure and temperature ranges, increasing the equilibrium temperature for the formation of hydrates, that is, shifting the region of hydrate formation to the right, consequently increasing it. In Figure 9 (A and B) it is possible to observe that all concentrations of isopropanol are maintain the same behavior, that is, always to the right of the curve of the uninhibited system. This behavior corroborates the previously existing experimental data present. in literature.

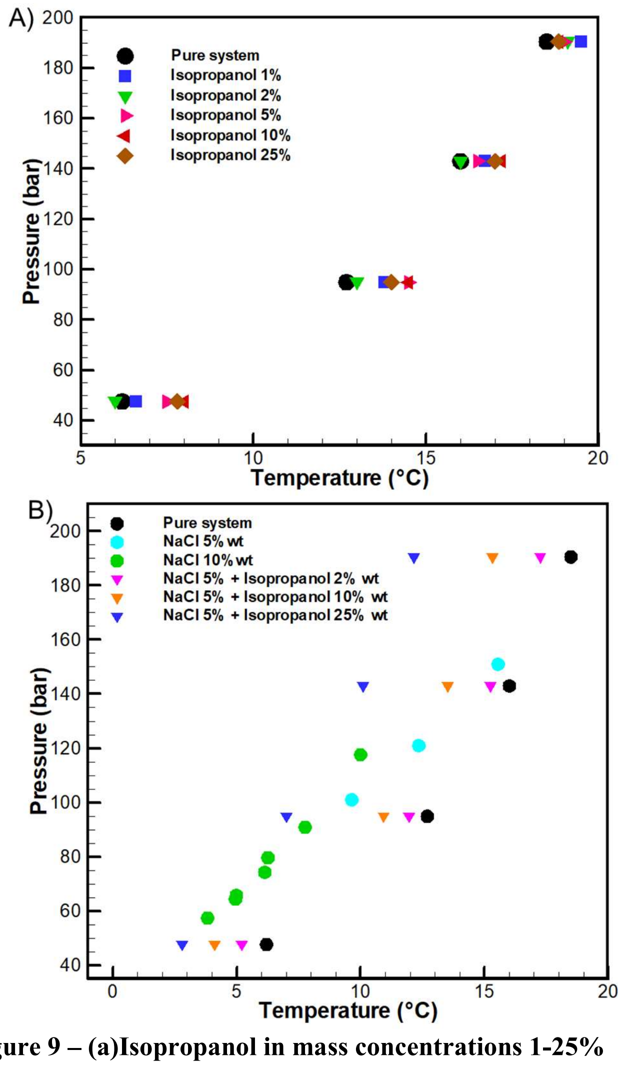

Figure 9 – (a)Isopropanol in mass concentrations 1-25%
(b) Isopropanol in mixtures systems. (With sodium chloride), ■ = Kakitani (2014).; ● = Present work (pure system); ▼= mixture of inhibitors

Since the inhibiting effect of sodium chloride alone is already established in literature, its influence on alcohol in the mixing system has been experimentally confirmed. This is due to the more frequent interactions of sodium chloride with molecules of water, which in turn allows isopropanol to remain in the interaction-free part molecular structure with hydrate cages. It is also suggested that given the interactions of salt with the structures, the possibility of non-occlusion of the isopropanol molecule next to the structure, leaving it free to act as an inhibitor, it occurs. In general, all mix data moved to the left of the system not inhibited. The 5% NaCl + 25% isopropanol concentration achieves the same inhibition effect of 10% pure NaCl. Therefore, for the mixture of inhibitors, when the formation gas is the methane, isopropanol behaves as a hydrate inhibitor together with NaCl.

3.4. Software comparison: isopropanol isolated systems

To carbon dioxide hydrates, the discrepancies between forecasts increase with increasing pressure and also, they are more evident at lower concentrations of isopropanol. For low concentrations (1 and 2%), Multiflash overestimates the effect of the inhibitor, and in contrast, for concentrations intermediate to high, the software underestimates the inhibitory effect of isopropanol. The NUEMhyd if gets closer to experimental points at low concentrations. At high pressures the program overestimates the inhibition effect at these concentrations, and returns a good agreement for intermediate to high concentrations (10-25%), returning low deviations. The program was found to be in agreement with the experimental data at low pressures (Figure 10-A).

To methane hydrates it´s possible to see that Multiflash could not predict for all concentrations have no inhibition or promotion effect, with all equilibrium curves in the same region of the uninhibited system, overlapping them. On the other hand, the NUEMhyd was able to predict the hydrate-promoting effects of isopropanol in various concentrations, as well as possible inversions of behavior. To the concentration of 1 and 2%, the isopropanol returns a veiled inhibition effect, that is, it tends to act as a hydrate inhibitor, but in the promotion region. According to Lee et al. (2013), this inversion of the experimental behavior is directly linked to the transition of the formed structure (sII to sI) (Figure 10-B).

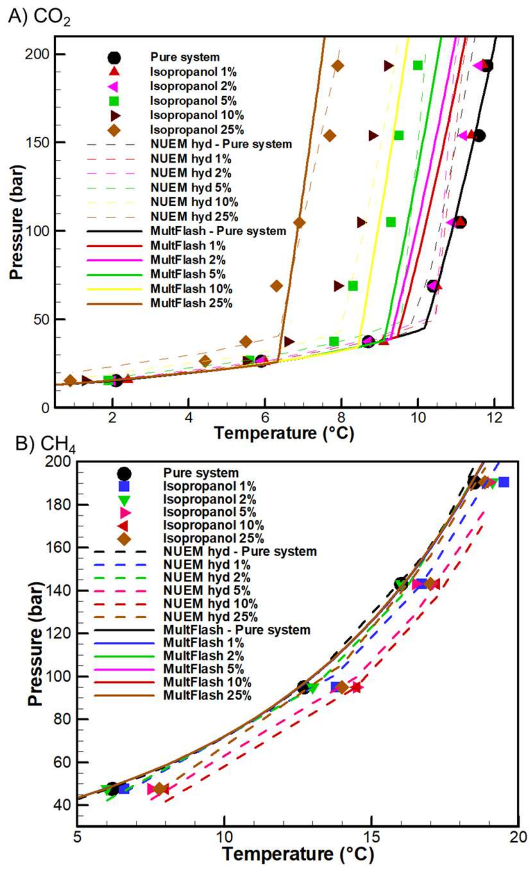

Figure 10 –Comparison with the softwares- (a) CO_2, (b)CH_4

3.5. Software comparison: isopropanol in mixture systems

For carbon dioxide hydrates, the inhibitor mixture data (isopropanol + NaCl), both software’s overestimated the inhibition power of the mixture, however, Multiflash got better results regarding this inhibition effect, shifting the curve to the left in a less accentuated, given the smaller distances between the experimental equilibrium curves.

We can highlight that for high concentrations of isopropanol in the mixture (data from 25%) software also overestimated the inhibition effect of isopropanol, distancing itself more clearly. It is noteworthy that below Q2 all data returned good agreement.

To methane hydrates, the inhibitor blend data for methane hydrate systems are arranged in Figure 11-B, MultiFlash was able to clearly differentiate the influence of NaCl in the system where the isopropanol is present, highlighting it as a thermodynamic inhibitor. It is also possible to observe that both softwares, for the experimental data, for a fixed concentration of 5% in mass of NaCl returned an inhibiting effect of the mixture on the methane gas hydrate system.

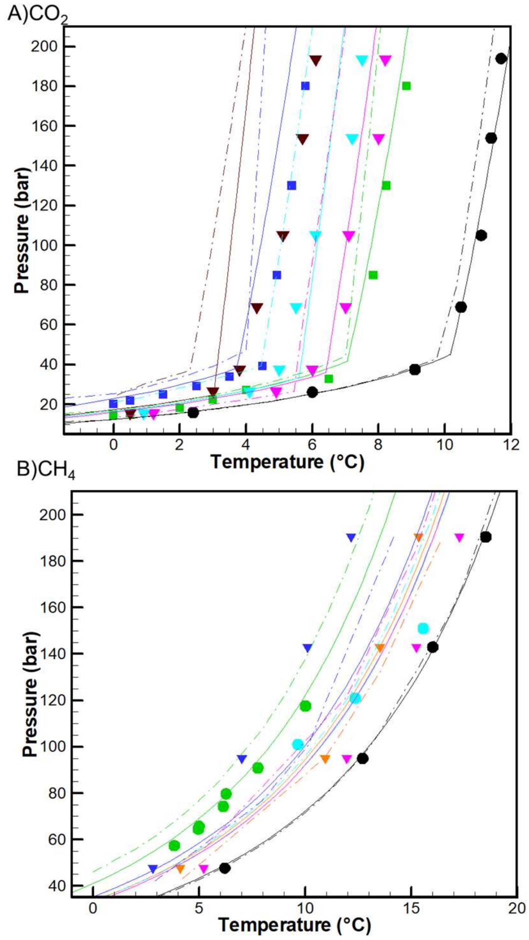

Figure 11 –Comparison with the softwares- (a) CO_2, (b)CH_4

4. CONCLUSIONS

The tests were mainly focused on obtaining experimental data from based on the model developed by Sirino *et al.* (2018) was. Overall, MultiFlash returned good agreement for most of thecsystems, however, NUEMhyd was able to more effectively predict the conditions of equilibrium for complex systems, such as high and low concentrations of inhibitors, high pressures and in possible inversion/transition scenarios of formed hydrate structures. For CO_2 hydrates isopropanol was characterized as an inhibitor thermodynamic and, for CH_4 hydrates, it behaved as a hydrate promoter, for all concentrations evaluated. Agreeing with the literature, the simulations performed revealed that there is a transition and/or structural coexistence from type sII to type sI, and that phenomenon can occur in scenarios where isopropanol is used in low concentrations.

5. ACKNOWLEDGEMENTS

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