EFFECTS OF EXPERIMENTAL FACTORS ON METHANE-PROPANE HYDRATE FORMATION THROUGH ISOCORRIC METHOD BY USING A PVT CELL

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RESUMO – Hydrate former system composed of methane-propane-water was studied at different experimental conditions using a PVT cell through isochoric method. This work evaluates the effects of some factors on hydrate formation, such as sub-cooling degree, mixing, multiple cycles and initial gas phase composition. These factors were verified to affect the rate of hydrate formation, the type and proportions of hydrate structures and the thermodynamic behavior during dissociation. The main results show preferential formation of structure I when mixing the system while structure II is favored at low sub-cooling and multiple cycles. Finally, the gas phase composition determines the type of structure which prevails during hydrate formation. Thus, these factors must be considered when comparing or designing experiments analysis using PVT cells.

1. INTRODUCTION

Gas hydrates are inclusion compounds formed by low weight gas molecules trapped in cavities known as "cages" constituted by water molecules linked through hydrogen bonds. Water in high pressure and low temperature environments added to the presence of natural gas, sometimes formed by anaerobic bacteria that decompose organic matter from the ocean floor, provide the essential conditions for the formation of gas hydrates.

The understanding of the mechanisms of formation or dissociation of these compounds has great scientific interest because of the large amount of hydrocarbons existing as gas hydrates and because of the important role of them on Earth's ecosystem (Aladko et al., 2002). On the other hand, the studies of the physical-chemical properties of gas hydrates demand considerable attention because they can imply on clogging of oil and gas transport pipes as they are an alternative energy source (Sloan et al., 2010).

Although the applications of gas hydrates are encouraging and their existence is abundant, it is necessary to know more about their growing and interaction with sediments present in the environment and how they could affect the environmental conditions during exploitation, especially in regions with extreme conditions of high pressures and low temperatures such as
in Brazilian pre-salt area, making evident the importance of studying these compounds.

Isochoric method is one of the most used for studying gas hydrates. A PVT cell is used and data of temperature and pressure are recorded along the thermodynamic procedure. However, the solid phase formed in specific thermodynamic conditions could present different properties according to the experimental protocols (Sloan et al., 2010). Thus, this work rises up some relevant factors that can imply to such differences and that should be taken in account when comparing literature data or planning experimental proceedings.

2. METHODOLOGY

The experimental configuration applied in this work was based on the UHP system available on the Hydrate Energy Innovation Laboratory at the Colorado School of Mines, that allows to analyze hydrates through isochoric method (HU et al., 2017). Figure 1 presents pictures from the apparatus, that features a gas booster, manual pressurizing valve, magnetic stirring and a thermal bath where a PVT cell is allocated inside. A sample of deionized water (~15ml) is added in a cylinder (~50ml) to be placed inside the PVT cell, shown below. Also, a baffle is accoupled inside this cylinder to break air bubbles and help liquid homogenization.

Figure 1 – Ultra-High-Pressure System and PVT cell configuration.

3. RESULTS

The system studied was composed by methane, propane and water. The results reveal the formation of two different hydrate structures. This is not foreseen by predictions in any gas phase composition range, since the propane molecules just fit on large cavities of structure sII. However, structure sI is formed simultaneously during cooling the system and probably it is occupied only by methane molecules. It is suggested due to the faster dissociation rate occurring close to structure sI equilibrium line. The equilibrium data were obtained using the van der Waals and Platteeuw model with the SRK equation of state, as implemented in CSMGem code Version 1.10. The simulations are represented by grey dashed lines in following graphs.

Sub-cooling: In Figure 2, the sub-cooling degree seems to affect the curve profile in the region between the hydrate equilibrium lines. A new stage of dissociation is noted in this area and it is marked by a new slope that is enhanced at the lower sub-cooling degree. It is reasonable to say that lower sub-cooling degrees favor sII hydrate formation once the sI hydrate zone is minimized. Thus, a higher amount of sII highlights the dissociation rate at this region.
Figure 2 – Sub-cooling effect on CH₄-C₃H₈ hydrate dissociation profile (92%mol CH₄).

Figure 3 – Mixing effect on CH₄-C₃H₈ hydrate dissociation profile (92%mol CH₄).

**Mixing:** Dissociation profiles shown in Figure 3 indicate that the ratio between methane and methane-propane hydrates is affected by stirring the system. Three consecutive runs were carried out, being that just the second run with mixing. The first and the third one present similar dissociation profiles, suggesting the structures formed in these cases had very similar ratio (sI/sII). By the other hand, the second run presents a different profile hinting a different proportion between structure sI and sII. Thus, according to these analysis, structure sI was favored in the presence of mixing because higher pressure is observed right after sI equilibrium line. It is reasonable considering more methane molecules come to be available to react with water under mixing conditions and also because methane hydrate requires less energy to be formed than double hydrates.

**Multiple Cycles:** In this analysis, the cycle was repeated but avoiding reaching equilibrium line of structure sII (Figure 4). At the first isotherm (6.8h at 292.85K), both hydrate formation on cooling and dissociation slope during the heating were notable. The second isotherm (33h at 304.85K) showed initially a high rate but then slowed down the hydrate formation (blue dashed circle). This behavior indicates there was still propane to induce sII formation during the first cooling, but instead, sI was also formed. The last isotherm (22.2h at 292.85K) shows hydrate formation at a slower rate as can be observed through the pressure dropping (orange dashed circle). Moreover, even after a longer time, the pressure did not drop so much as during the first isotherm, that only lasted 6.8h. Indeed, subsequent run seems to favor conversion from sI to sII, which is suggested by the smaller slope indicated by the green arrow. Although sI is faster to be formed, sII is the most stable structure to this system and it may be favored in latter runs due to the presence of crystals formed previously.

**Gas Phase Composition:** The gas composition has an important role on the type and ratio of structures going to be formed. The first sample shown in figure 5 has the highest propane content and suggests no sI was formed once the slope related to dissociation appears 4K far from sI equilibrium line. In the next sample (92% of methane) one can clearly note the dissociation started immediately before sI equilibrium line, evidencing the presence of both sI and sII. The last sample changed the profile again and the dissociation looks like a more continuous process. It is because most of hydrate formed in this case constitutes structure sI.
4. CONCLUSION

This work points out some effects of experimental factors on thermodynamic behavior of methane-propane hydrates formed through isochoric method by using a PVT cell. In this specific system, two different structures are initially formed. Besides the expected structure (sII), the other one (sI) is composed only by methane molecules, since propane does not fit on any cavity of this structure. Each factor cited in this work showed to affect the hydrate dissociation profile, which is defined according to the existing structures. At lower sub-cooling degrees, two different slopes during the heating are enhanced and can be related to each hydrate structure dissociation. Mixing favors the formation of sI since higher increase in pressure is observed right after sI equilibrium line. Finally, consecutive runs lead to the conversion of sI to sII, that is a more stable configuration for this system. Besides, latter run presented lower rate of hydrate formation hinting the structure sI takes place mainly at initial stages. Finally, the gas composition has a crucial role in the type and ratio of structures going to be formed.

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