



## EXPERIMENTAL PHASE EQUILIBRIA OF CARBON DIOXIDE AND METHANE HYDRATES IN THE PRESENCE OF 2-PROPANOL AND SODIUM CHLORIDE

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### Abstract

In oil exploration, 2-propanol is a chemical often used during stimulation and workover. However, some reports point out that 2-propanol can promote hydrate formation, especially in systems with either CH<sub>4</sub> or CO<sub>2</sub> acting as auxiliary gas. New experimental data for phase equilibrium of inhibited carbon dioxide and methane hydrates were obtained by the isochoric experimental method in a high-pressure cell, for pressures between 20 and 260 bar, under concentrations ranging from 5 to 25 wt% of 2-propanol. New experimental data on mixtures of 2-propanol and NaCl (5 wt%) were also obtained in order to evaluate the behavior of this alcohol in saline mixtures. It was observed that 2-propanol has a hybrid behavior, highly dependent on the gas system composition. 2-propanol has been characterized as a CO<sub>2</sub> hydrates inhibitor and a CH<sub>4</sub> hydrates promoter. In salt mixtures, 2-propanol is a thermodynamic inhibitor for both gases and in concentrations higher than 10 wt%, 2-propanol had a satisfactory inhibition effect.

### Keywords

hydrates, carbon dioxide, methane, NaCl, 2-propanol,

### Introduction

Gas hydrates are non-stoichiometric crystal structures that can confine guest molecules into well-defined host lattices built upon hydrogen-bonded water molecules formed under conditions of low temperature and/or high pressure. These structures can be arranged in three groups: structure I (sI), structure II (sII), and structure H (sH), which differ in shapes or sizes of the cages formed[1][2].

In oil and gas production, the formation of hydrate plugs can lead to serious pipeline blockages, causing handsome economic losses and safety issues. The injection of thermodynamic inhibitors is widely used to avoid hydrate formation in the pipelines[3]. By adding thermodynamic inhibitors, such as alcohols (ethanol, methanol, etc.) and glycols (MEG, DEG, TEG, etc), the hydrate formation envelope is shifted to an operationally safe condition. These compounds act by changing the water activity through hydrogen bonding with the H<sub>2</sub>O molecules [4].

In oil and gas production, 2-propanol is a product commonly used to help in a rapid recovery of injected fluids. In recent years, this alcohol has been used to prevent hydrate formation or to dissociate already formed hydrates, whose combination with hydrochloric acid for hydrate

inhibition during gravel packing in the Gulf of Mexico was reported[5][6]. Other studies document that 2-propanol acts as a low-dosage kinetic hydrate inhibitor used in North Sea operations, and is present in formulations as a scale inhibitor solvent or noxious gas sequestrants [7].

Recently, the offshore exploration and production of gas and oil has moved to harsher scenarios, such as the Brazilian pre-salt. Therefore, the umbilical lines emerged as a practical way to transport chemicals (such as 2-propanol) to the bottom of the well or to strategically-positioned locations along the production line, and at opportune times[8]. In some scenarios, aqueous solutions of chemicals can be transported by the umbilical under the risk of hydrate formation, which may compromise the operation of this auxiliary line.

The inhibition potential of 2-propanol with regard to methane hydrates has been evaluated. Østergaard et al.[9] observed that 2-propanol acts as hydrate promoter, in concentrations of 0.10 to 0.25 mass fraction. These results agreed with the model developed by the authors. Also, it was detected that the 2-propanol promotes the formation/transition to the sII structure[9].

For CO<sub>2</sub> hydrates in the presence of the 2-propanol and 1-propanol in aqueous solutions of concentrations between 5 to 10 wt% fractions, under pressures up to 41.0 Mpa, the behavior is the opposite when compared to methane hydrate. In these scenarios both alcohols act as an important thermodynamic inhibitor for CO<sub>2</sub> hydrate[10];[11]. Other studies for intermediate concentrations of up to 10wt % of isopropanol reported that it behaves as a thermodynamic inhibitor of CO<sub>2</sub> hydrates, however, contrary to what was originally supposed, a double hydrate of isopropanol and CO<sub>2</sub> does not occur; only a single CO<sub>2</sub> hydrate can be obtained in the studied systems at the conditions under consideration[12].

The focus of this work is to bring new experimental data relating to CO<sub>2</sub> and CH<sub>4</sub> hydrates in 2-propanol systems and in the presence of mixtures of inhibitors. In an attempt to fulfill some of these gaps found in the literature, the present study investigates the phase equilibrium of hydrates (carbon dioxide and methane) in aqueous 2-propanol and sodium chloride systems by an isochoric experimental methodology using a high pressure cell.

Indeed, it was observed that for a higher concentration of 2-propanol, a greater inhibition effect with regard to CO<sub>2</sub> hydrates was achieved. For CH<sub>4</sub> hydrates, 2-propanol acted as a hydrate promoter.

## Methodology

### Experimental apparatus

A high pressure cell was used to determine the phase equilibrium of CO<sub>2</sub> and CH<sub>4</sub> hydrates inhibited by 2-propanol and mixtures. Figure 1 shows a simplified layout of the experimental apparatus. The structure has two supply lines, one of which is coupled to a syringe pump and another one arranged in a quick coupling, a communication line with the high-pressure cell, and a purge line for the gas outlet.

The apparatus is composed of a gas cylinder (A) which supplies the syringe pump (Teledyne ISCO 260D) (B) which is connected to a set of valves (C) that, when necessary, is coupled to a vacuum pump (D). The apparatus also contains a recirculation thermostatic bath (Polyscience, PP15R-40-A11B) (E) – used to control the temperature of the cell, circulating the coolant through the cell heat exchanger (F), and data receiver (H). The distribution line controlled by the set of valves, as described above, maintains the dynamic methodology isochoric. Finally, the high pressure cell, consists of a steel pressure vessel built in 316 stainless steel, with a maximum capacity of 34.86 mL, an internal diameter of 17.6 mm and a length of 143.3 mm. The cell's frontal chamber is assisted by two sapphire windows used for visualization and illumination. A magnetic stirrer is used in order to ensure the homogenization of the experimental system. The vacuum pump is

used to remove the air from the pipe and the dissolved air in the aqueous phase. Data are monitored by pressure (EJX510A - Yokogawa) and temperature (YTA-710 de Yokogawa RTD) transducers and are collected and stored on a computer (H).



Figure 1. Schematic representation of the experimental apparatus for phase equilibrium measurement

### Experimental procedure

The experimental procedure adopted for all investigations consisted in the system cleaning and set up, followed by the insertion of chemicals and the experimental tests and measurements. After the liquid is inserted, a depressurization is applied with the vacuum pump, in order to remove the air which might be present in both the lines and cell. The second step consists in feeding the chemicals of the test. The gas was injected via a syringe pump (CO<sub>2</sub> or CH<sub>4</sub>). Then, the gas was injected at a low flow rate. After the desired pressure was achieved, a leak test was carried out. At this point, the magnetic stirrer is activated for homogenizing the mixture.

### Results and Discussion

To determine the equilibrium conditions of carbon dioxide and methane hydrates, experiments using an isochoric static-synthetic methodology were carried out. Those experiments were performed with and without the presence of 2-propanol and sodium chloride mixtures. Different concentrations were tested to investigate the shifting effect of the phase equilibrium curve, that is, the hydrate inhibition or promotion potential.

Table 1 shows the grid test of the experiments described in this work.

Table 1. Test Matrix

Initial Pressure		20; 30; 40; 100; 170; 210; 260 bar
CO <sub>2</sub>	Pure system	Pure water
	x mass% 2-propanol	5; 10; 25
	5 mass% NaCl + x mass% 2-propanol	5; 10; 25
Initial Pressure		50; 100; 150; 200 bar
CH <sub>4</sub>	Pure system	Pure water
	x mass% 2-propanol	5; 10; 25
	5 mass% NaCl + x mass% 2-propanol	2; 10; 25

2-propanol and NaCl were evaluated as thermodynamic hydrate inhibitors for CO<sub>2</sub> and CH<sub>4</sub>. As discussed in the first section, these substances act by interacting with water molecules, decreasing their availability to form hydrates in such a way that their presence is expected to cause a decrease in the equilibrium temperature for the same pressure. The phase equilibrium data for the systems of 2-propanol in CO<sub>2</sub> + H<sub>2</sub>O were obtained. To assess the inhibiting effect of 2-propanol, mass concentrations of 5%, 10%, and 25% were used. Each experiment was planned to be performed only once due to the time taken to survey each experimental point, except the points performed in duplicate, as indicated in Table 4. The slow heating rate used for all experiments was chosen in such a way that at each time step, the pressure reach stability, demonstrating that the system is in equilibrium. The experimental tests lasted, on average, between 40 and 72 hours for each point.

Figure 2 shows inhibited equilibrium data for carbon dioxide hydrates with 2-propanol. As expected from an alcohol and according to the literature review, propanol acted as a thermodynamic inhibitor, decreasing the formation equilibrium temperature for hydrates.

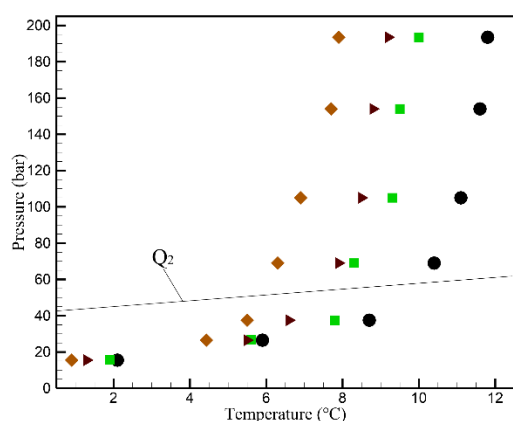


Figure 2. Results of phase equilibrium data of CO<sub>2</sub> hydrates in 2-propanol presence: fresh water (black circles), 5 wt% (green square), 10 wt% (purple right triangles) and 25 wt% (brown diamond).

It was observed that higher concentrations of 2-propanol caused greater inhibition effects. Figure 3 shows equilibrium data for methane hydrates in the presence of 2-propanol. According

to the literature review, 2-propanol proved to be a thermodynamic promoter of methane hydrates within the investigated pressure range (50 to 200 bar), increasing the equilibrium temperature for hydrate formation and shifting the hydrate formation region to the right[13]. It is possible to observe that all 2-propanol concentrations show the same behavior, that is, always to the right of the curve of the uninhibited system.

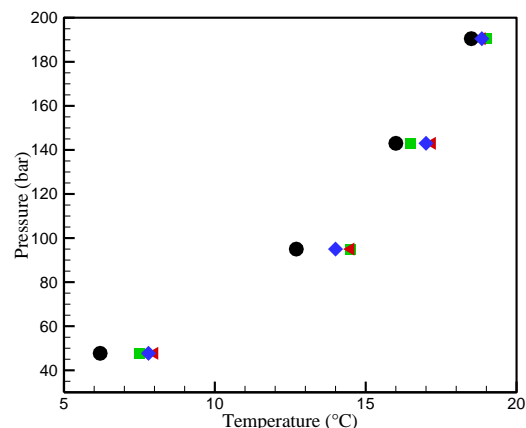


Figure 3. Results of phase equilibrium data of CH<sub>4</sub> hydrates in 2-propanol presence: fresh water (black circles), 5 wt% (green square), 10 wt% (red right triangles) and 25 wt% (brown diamond).

Results for the systems containing the thermodynamic inhibitor mixture, further information and discussions will be available in the full paper.

## Conclusions

An isochoric experimental procedure was performed in order to investigate the influence of 2-propanol in the phase equilibrium of dissociative systems of CO<sub>2</sub> and CH<sub>4</sub> hydrates.

It was observed that 2-propanol has a hybrid behavior, highly dependent on the gas system composition. It can be concluded that 2-propanol has been characterized as an inhibitor of CO<sub>2</sub> hydrates and a promoter of CH<sub>4</sub> hydrates.

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## Responsibility Notice

The authors declare no competing financial interest

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