Fluid Phase Equilibria 413 (2016) 10–21

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Experimental procedure and results to measure the composition of gas hydrate, during crystallization and at equilibrium, from N_2–CO_2–CH_4–C_2H_6–C_3H_8–C_4H_{10} gas mixtures

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ARTICLE INFO

Article history:
Received 7 July 2015
Received in revised form
12 October 2015
Accepted 14 October 2015
Available online 19 October 2015

Keywords:
Clathrate hydrates
Experimental study
Thermodynamics
Phase equilibria

ABSTRACT

Mixed Clathrate hydrates are an important issue in many fields, like flow assurance in the oil industry, as well as gas capture and storage, air conditioning, etc …

Usually, studies of gas hydrates from hydrocarbon gas mixtures do not mention the volume of hydrate, nor the hydrate composition, and ternary or quaternary mixtures are not considered. Also, data involving propane and butane are limited.

Therefore, we suggest both an experimental and modeling study of mixed clathrate hydrates from N_2–CO_2–CH_4–C_2H_6–C_3H_8–C_4H_{10} gas mixtures, in temperature range of [0.8–19 °C] and pressure range of [1.4–66 bars]. The experimental work provides 78 equilibrium points. Two procedures were used to perform crystallizations. The main procedure (71 equilibrium data) corresponds to a method at high crystallization rate (high supersaturation, or high ΔP). The first objective is to study the gas hydrates formation in usual dynamic conditions (start-up or reboot of an oil exploitation). The second method, 7 data, corresponds to a low rate of crystallization. This second objective is to investigate the impact of the speed of crystallization on the final equilibrium. For both procedures, P-T data are given, as well as the compositions of each phase at equilibrium.

At last, thermodynamic modeling is used to compare the experimental results of both procedures. Kihara parameters of N_2, CO_2 and CH_4 are taken from the literature, while parameters for C_2H_6 are regressed and given in this work.

Results show a better agreement of the thermodynamic modeling with experimental study for pure gas hydrate and mixed gas hydrates at low crystallization rate. This observation suggests that mixed gas hydrates might form at thermodynamic equilibrium only at low crystallization rate.

1. Introduction

Gas hydrates, or clathrate hydrates, are components crucial components in many fields. Flow assurance issue is probably the reason why they were so widely studied in the past decades [1]. Exploration and exploitation of methane hydrate buried in permafrost and deep-sea is also a major issue [2], as well as gas capture and storage (mainly CO_2) [3].

Pipe-line plugging in the oil industry is the start of the study, brought by TOTAL SA about hydrocarbon gas mixtures. Indeed, the interest for unconventional oil resources is growing (mainly in deep-offshore). In this situation, hydrate risk is significant and has to be controlled (zero tolerance policy).

Therefore, to study the hydrate risk of formation, experimental data as well as thermodynamic modeling, are essential. But, if gas hydrate from hydrocarbon gas mixtures has been widely studied, few data involving propane and butane are available. Moreover, these studies do not provide the hydrate volume and water consumption. Sometimes, a modeling approach is suggested using classic van der Waals and Platteuw theory [4]. The use of such

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http://dx.doi.org/10.1016/j.fluid.2015.10.022
0378-3812/

theory usually involves parameters, the so-called Kihara parameters. However, these parameters are very dependent on the authors and on the quality of the experimental data used (both equilibrium data and reference thermodynamic properties). We showed in a previous paper such differences (ε/k from 165 to 175 for CO_2 as example) [5]. This is why acquiring accurate and complete data is an essential part of the modeling work. But, obtaining satisfying results can be tricky if hydrate crystallization involve kinetic considerations.

In this work, gas hydrates from CO_2–CH_4–C_2H_6–C_3H_8–C_4H_{10} gas mixtures are studied. To go further in the experimental approach, the procedure used provides not only the measurement of the classic Pressure/Temperature data at equilibrium, but also the hydrate composition and volume.

To evaluate the influence of the speed of crystallization on the final state, two procedures were used: at high crystallization rate (high driving force, for example at the start-up of a well), and at low crystallization rate (low driving force, corresponding to steady state exploitation). 12 Experiments were performed providing 78 equilibrium points. 71 data were obtained from quick crystallization, and 7 from slow crystallization experiments.

In the end, experimental results were compared to the classic van der Waals and Platteuw model. Ethane Kihara parameters needed to be calculated. Parameters of propane and butane could not be regressed from pure gas hydrates.

2. Gas hydrates

Gas hydrates, or clathrate hydrates, are ice-like crystalline compounds composed of molecules of water and small molecules (usually gaseous at standard conditions). They present different polymorphic structures depending on the guest molecules. Three main structures were identified: SI, SII and SH ([6]). Table 1 presents a brief description of classic clathrate hydrate structures.

These compounds may be formed at low temperature and high pressure. The liquid-hydrate phase diagrams depend on the structure (I, II, H) and guest molecules, see Fig. 1 as example.

3. Materials and methods

3.1. Experimental set-up

The experimental set-up (Fig. 2) allows the measure of hydrate equilibria. From temperature and pression measurements, as well as gas and liquid sampling, the equilibrium state can be completely determined: compositions and masses of each phase in the reactor. The apparatus composed of an instrumented batch reactor (Autoclave, 2.36 L). This reactor is fed with pure gas, or prepared gas mixture. A HPLC pump (JASCO-PU-1587) is used to inject the liquid phase (water + $LiNO_3$, used as tracer for the determination of the water concentration). A cryostat (HUBERT CC-505) keep a constant temperature in the reactor (0.02 °C accuracy), and two sapphire windows (12 cm × 2 cm) are placed on each sides of the reactor to keep an eye on the crystallization. The reactor is stirred on the upper side (vapor phase) and lower side (liquid/hydrate phase). The pressure, as well as the temperature on the upper/lower side, is monitored online with a data acquisition system (Pt 100, accuracy 0.02 °C, pressure accuracy 0.1 bar).

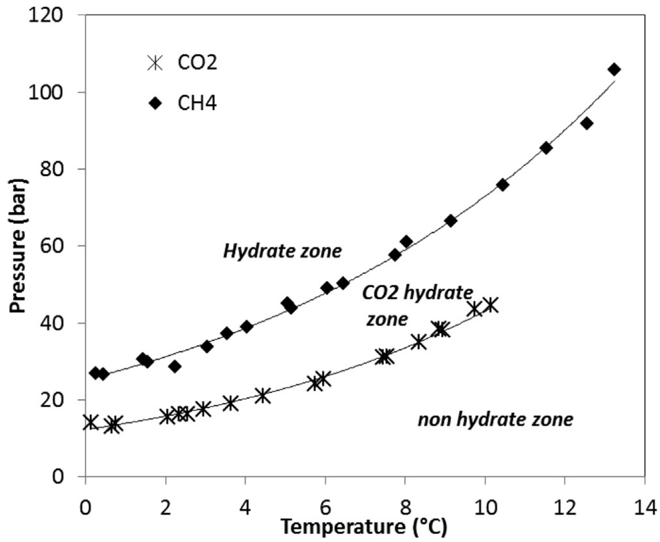


Fig. 1. Experimental CO_2 and CH_4 P-T hydrate equilibria diagrams [7–9].

To determine the composition of each phase at equilibrium (by mass balance calculations), the gas phase composition is sampled (ROLSI™) and injected in a gas chromatograph (VARIAN model CP-3800 GC with a 50 m PORA BOND Q column). A few μm^3 is taken each time. Helium is used a carrier gas in the GC. The liquid phase is analyzed offline by ionic chromatography (DIONEX ionic exchange chromatograph). A simple valve is used to sample the liquid phase (water + $LiNO_3$).

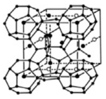
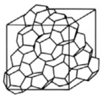
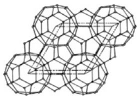
3.2. Experimental procedure at high crystallization rate

The first experimental procedure is the same as in previous studies [5]. Fig. 3 shows the crystallization and dissociation process. This procedure is performed at high crystallization rate (or at a high supersaturation). For gas hydrates this means high ΔP (or high ΔT).

At the beginning, the reactor is cleaned and emptied (40 min). Then, the cell is filled with gas mixture, either by direct injection of the pure gases or from a prepared bottle.

The pressure is measured, and the temperature is then set to 0–1 °C (internal regulation of the cryostat). The gas composition in the cell is checked with GC analysis at the beginning and before any

Table 1
Structure of gas hydrates [6].

	SI		SII		SH		
							
Cavity(*)	5^{12}	$5^{12}6^2$	5^{12}	$5^{12}6^4$	5^{12}	$4^35^66^3$	$5^{12}6^8$
Type of cavity	1	2	1	3	1	5	4
Number of cavity	2	6	16	8	3	2	1
Average cavity radius (nm)	0.395	0.433	0.391	0.473	0.391	0.406	0.571
Variation in radius,%	3.4	14.4	5.5	1.73			