Contents lists available at ScienceDirect

J. Chem. Thermodynamics

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

Bulk liquid and gas mole fraction measurements during hydrate growth for the CH₄ + CO₂ + H₂O system

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ABSTRACT

Gas and liquid mole fraction were experimentally obtained for the $CH_4 + CO_2 + H_2O$ system at four different time intervals during hydrate growth. In order to validate the procedure, equilibrium mole fractions were also obtained and satisfactorily compared to literature values. Using a 70.0% CH_4 – 30.0% CO_2 loading composition in combination with a 1.6 MPa driving force at 274 K, results showed that both the liquid and gas mole fraction of methane and carbon dioxide were independent of time during the early stages of growth. For comparison purposes, samples were also obtained during the induction period. After the nucleation event, methane liquid mole fractions dropped below induction values while no change was observed for carbon dioxide. It is therefore postulated that methane consumption is favored during the early stages of growth. The rates of crystal growth were acquired and in parallel with all other parameters obtained experimentally, were proven critical to understand multicomponent gas hydrate kinetics.

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1. Introduction

Gas hydrates are the consequence of a phase change, resulting in a solid state where guest molecules become enclosed by three-dimensional water molecule structures. These cavities form through hydrogen bonding and only interact with their guest through weak van der Waals forces. Molecules capable of forming clathrates include methane, ethane, carbon dioxide, nitrogen as well as volatile liquids like neohexane [1]. As with any phase transition, thermodynamics dictate favorable conditions, which in the case of gas hydrates, are moderate temperatures and high pressures.

This crystalline compound has been recognized as a potential energy resource due to significant natural deposits in ocean seafloors and permafrost regions containing valuable hydrocarbons such as methane [2]. Conversely, gas hydrates have also been showed to form inside natural gas pipelines, hindering flow assurance [3]. Kinetic and thermodynamic inhibitors were as a result, developed to prevent these masses from becoming safety concerns. As such, these inhibitors are applied in environments where not one but many gas components are present stressing the importance of multicomponent gas hydrate systems. Novel technologies are also being developed such as flue gas separation [4], carbon

dioxide sequestration [5,6] and transportation of natural gas [7]; all examples of cases where several gas components populate systems.

Analogous to crystallization processes, gas hydrate formation requires the liquid phase to be supersaturated with a guest in order to provoke a nucleation event. Proposed by Bergeron and Servio, the driving force for hydrate growth for simple gas hydrate systems (one guest component) is described as the difference between the bulk liquid mole fraction (x^B) and the solubility (x^{HL}) under two-phase H-Lw equilibrium, both at experimental temperature and pressure [8]:

$$\frac{dn}{dt} = \frac{V_L \rho_w}{MW_w} \pi \mu_2 k_r (x^B - x^{HL}) \tag{1}$$

where V_L is the volume occupied the solution, ρ_w the density of water, MW_w the molecular weight of water, μ_2 the second moment of the particle distribution [9] and k_r the intrinsic rate constant.

For this model to be established, several parameters were obtained experimentally, including bulk liquid mole fractions and mole consumption measurements *(dn/dt)* of systems using gases such as methane and carbon dioxide [8]. The goal of this study is to extrapolate this work to multicomponent systems to build the foundation for future multicomponent kinetic models.

As both methane and carbon dioxide have been extensively investigated as simple hydrate systems due to their numerous applications including carbon dioxide sequestration, their mixture

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is a relevant selection for the proposed work. Kinetic studies on the $CH_4 + CO_2 + H_2O$ system have already been documented using gas chromatography, NMR and Raman spectroscopy but never through liquid mole fraction measurements during growth [10–12]. To the best of our knowledge, this work represents the first attempt at characterizing the liquid phase of any multicomponent gas hydrate system through mole fraction measurements during growth. To complete the analysis, the gas phase is analyzed in parallel through gas chromatography. In addition, solubility measurements, bulk liquid phase mole fractions during induction as well as mole consumption trends are obtained.

2. Experimental

2.1. Experimental apparatus

The experimental apparatus used for this study is illustrated below by Fig. 1. A stainless steel 316 crystallizer is equipped with two polycarbonate windows allowing for visual inspections. To indirectly control its temperature, it is submerged in a bath holding mixture of glycol-water; itself controlled by a Neslab RTE chiller. Three small gas cylinders are submerged which assist in providing isobaric conditions during kinetic experiments. The reservoir, set at a pressure above experimental conditions, provides gas to the crystallizer through a Baumann 51000 Low Flow control valve. The two other cylinders serve as biases providing accurate pressure readings for both the reservoir and the crystallizer. To reduce heat and mass transfer limitations inside the crystallizer, a magnetic stir bar is used which is spun by rotating magnets. In order for the experimental data to be comparable, only one single gas mixture with mole fractions of 0.700 for methane and 0.300 for carbon dioxide was chosen for the study (absolute analytical tolerance of +/-0.0002), purchased from MEGS. Water previously treated by McGill University through reverse osmosis, was injected in the crystallizer with a positive displacement pump (Oilphase-DBR, Schlumberger). Less than 10 ppb (equivalent to a mass fraction of 10^{-8}) of total organic content was present in the liquid while having a conductivity of 10 μS. Temperature and pressure readings were recorded through a National Instruments® data acquisition system. Omega RTD probes (±0.1 K) were used for temperature measurements while pressure was monitored via Rosemount

pressure transducers with a span of 0–14 MPa and accuracy of ±0.065% of the given span. Gas and liquid samples were extracted using sample cylinders purchased by Swagelok. In order to prevent the inclusion of hydrate particles during sampling, an in-line Norman filter was installed. Gaseous mole fractions were analyzed through a gas chromatography (Varian CP-3800) while a digital gasometer (Chandler Engineering) was used to evaluate the volumetric amount of gas dissolved in liquid samples.

2.2. Experimental procedure

In order to provide insights into multicomponent gas hydrate kinetics, liquid and gas samples were extracted during hydrate growth at 0, 5, 10 and 15 min after nucleation. Additional samples were obtained during induction and at equilibrium. Three replicates per conditions were acquired during growth where every single experiment yielded one liquid and one gas sampling. Hence, after each experiment, the crystallizer was emptied and the procedure described below was repeated.

For these results to be comparable and repeatable, experimental conditions during hydrate growth had to be kept constant in order to yield a constant driving force. In simple gas hydrate systems, typically temperature is controlled and pressure is kept constant at a certain value above the three-phase equilibrium line as illustrated by Fig. 2. However, in a binary gas system, one more degree of freedom is present, bringing the degree of freedom of the system to two. Hence, a three-dimensional plane now represents all equilibrium conditions instead of a simple two-dimensional line, as illustrated by Fig. 3. This means that in addition of having temperature constant, another variable has to be maintained for the experimental conditions to be locked in the same position above the equilibrium plane.

The gas phase composition was used as the additional intensive property. Although it cannot be used to define the two-phase H-Lw solubility, it can be used to confirm consistent operating conditions during growth. This explains why gas phase compositions were obtained in parallel with liquid mole fractions measurements. In this work, operating conditions during hydrate growth were at 3.9 MPa, 274 K and gas mole fractions of 0.8 for methane and 0.2 for carbon dioxide. These operating conditions are 1.6 MPa higher than the location on the three-phase equilibrium that shares the same temperature and gas phase composition as illustrated by
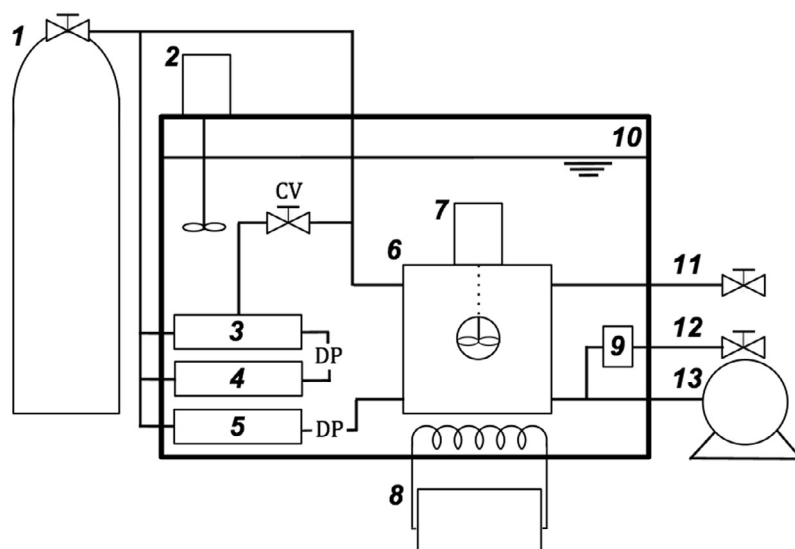

Fig. 1. Experimental setup: (1) gas cylinder, (2) liquid bath stirrer, (3) reservoir, (4) reservoir bias, (5) crystallizer bias, (6) crystallizer, (7) crystallizer stirrer (8) chiller, (9) filter, (10) bath, (11) gas sampling port, (12) liquid sampling port (13) displacement pump.