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CO_2 and CH_4 mole fraction measurements during hydrate growth in a semi-batch stirred tank reactor and its significance to kinetic modeling

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ABSTRACT

A new experimental technique has been developed to measure the mole fraction of the gas hydrate former in the bulk liquid phase, at the onset of hydrate growth and thereafter, in a semi-batch stirred tank reactor. The mole fraction of carbon dioxide and methane in the bulk liquid phase was obtained for the first 11 and 13 min of the growth stage, for the carbon dioxide–water and methane–water systems respectively. Experiments were conducted at temperatures ranging from 275.3 K to 281.4 K and at pressures ranging from 2017 kPa to 4000 kPa for the carbon dioxide–water system, while temperatures ranging from 275.1 K to 279.1 K and pressures ranging from 3858 kPa to 6992 kPa were investigated for the methane–water system. The mole fraction of carbon dioxide in the bulk liquid phase was found to be constant during the growth period, varying on average by 0.6% and 0.3% at 275.4 K and 279.5 K. Similarly, the mole fraction of methane in the bulk liquid phase was found to remain constant during the growth stage, varying on average by 2.0%, 0.8% and 0.2% at 275.1 K, 277.1 K and 279.1 K respectively. The mole fraction of the gas hydrate former in the bulk liquid phase was also found to increase with pressure and decrease with temperature, while remaining greater than its hydrate-liquid water equilibrium value. As a result, an alternate formulation of a hydrate growth model is proposed.

1. Introduction

Gas hydrates, or clathrate hydrates, are non-stoichiometric crystalline compounds in which a gas or a volatile liquid molecule suitable for hydrate formation is enclosed in a network consisting of water molecules linked together through hydrogen bonding. The presence of the gas molecule stabilizes the water lattice via weak van der Waals forces. Three naturally occurring hydrate structures have been reported in the literature, including structure I (sI), structure II (sII) and structure H (sH) [1]. In particular, carbon dioxide and methane form structure I hydrate, while propane and neohexane (in the presence of methane) form structure II and structure H hydrate respectively. Considerable research is being conducted on gas hydrates due to their potential applications, including naturally occurring methane hydrates as an alternate energy source [2], storage and transportation of natural gas or liquefied petroleum gases in hydrate form [2,3], as well as carbon dioxide sequestration as a means to mitigate the global warming effect [2]. Such promising new technologies are reasons why kinetic studies should be further investigated. In particular, an accurate value for the reaction rate constant of hydrate formation is required for proper reactor design aimed at large-scale hydrate production. The reaction rate constant is the sole parameter affecting any reactor throughput and conversion that remains constant upon scale-up, as both heat and mass transfer effects will change. Recently, Ribeiro and Lage [4] performed an extensive literature review of the existing hydrate growth kinetic models. Some of the most well-known models include the pioneering work of Englezos et al. [5,6], as well as the model of Skovborg and Rasmussen [7]. The former can be used to determine the reaction rate constant of hydrate formation, while the latter limits hydrate growth to a mass transfer problem, without any reaction rate constant. More recently, Hashemi et al. [8] have proposed a new driving force for hydrate growth. Their driving force is based on the concentration of the gas hydrate former under hypothetical vapor–liquid water equilibrium, at the experimental temperature and experimental pressure, and that under hydrate-liquid water equilibrium, again at the experimental temperature and experimental pressure [8]. Following this, Bergeron and Servio [9] have incorporated this new driving force into a modified version of the model of Englezos et al. [5], resulting in a new kinetic model for hydrate growth aimed at determining the reaction rate constant of hydrate formation. Nevertheless, all these mod-

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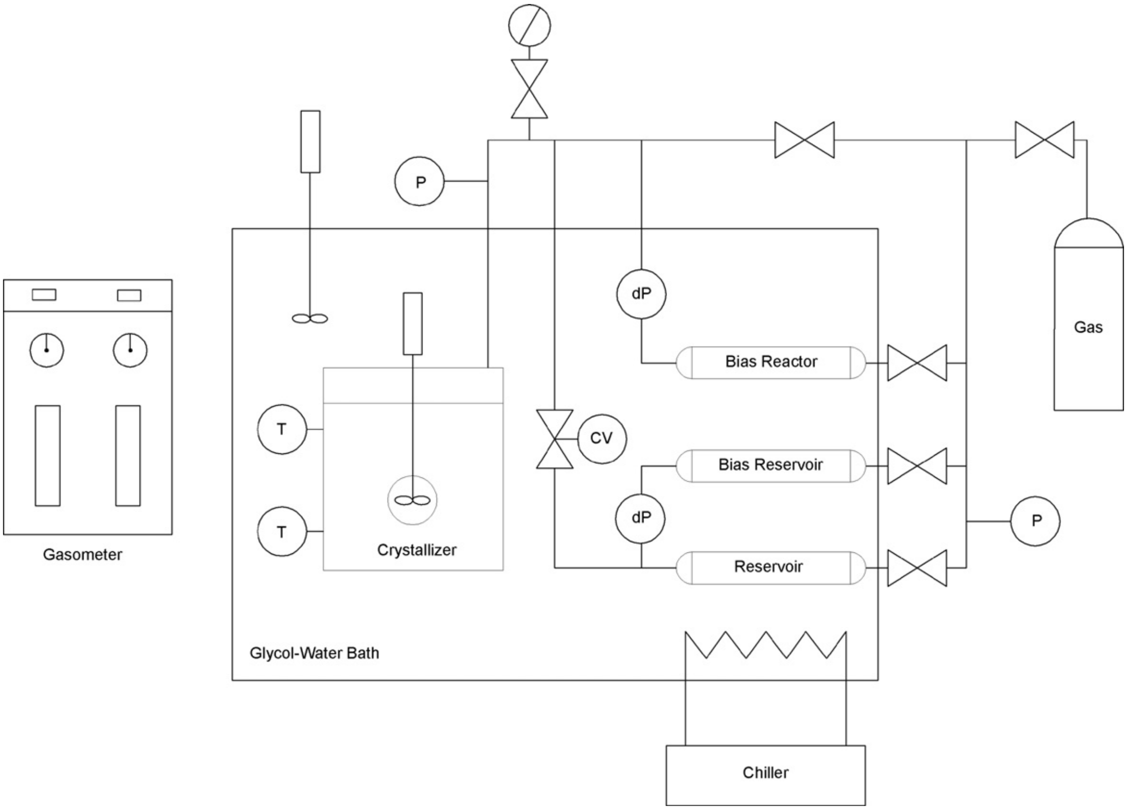

Fig. 1. Simplified schematic of the experimental setup.

els need to account for the dissolution rate at the vapor–liquid water interface, which its determination has been shown to be controversial. In their work, Bergeron and Servio [9] hypothesized that the dissolution rate at the vapor–liquid water interface was enhanced, compared to the value obtained from solubility experiments, due to the presence of hydrate particles during growth. Kluytmans et al. [10] also concluded that the presence of particles in a system could readily increase the dissolution rate at the vapor–liquid water interface by creating turbulence and reducing the effective boundary layer thickness, which would increase the mass transfer coefficient. Even though several authors have measured the solubility of carbon dioxide [11,12,13] and methane [14,15,16,17,18] in the liquid phase under hydrate-liquid water equilibrium, to the best of our knowledge, there is no experimental data regarding the mole fraction of the gas hydrate former in the bulk liquid phase at the onset of hydrate growth and thereafter. The work of Teng and Yamasaki [19] is the only reference to solubility measurements approximating the solubility of carbon dioxide in the metastable absence of hydrates, as reported by Ohmura and Mori [20]. In addition, Hashemi et al. [8] have shown from a modeling point of view and using the work of Clarke and Bishnoi [21], that the bulk concentration of the gas hydrate former does not change significantly with time after the onset of growth. In their analysis, they assumed that at the onset of growth, the concentration of carbon dioxide in the bulk liquid phase dropped from its turbidity value to its equilibrium value [8]. To assess these issues from an experimental point of view and to eliminate the need to rely on uncertain values for the dissolution rate at the vapor–liquid water interface, an alternate formulation of the model of Bergeron and Servio [9] is suggested, based on experimental measurements of the mole fraction of carbon dioxide and methane in the bulk liquid phase at the onset of hydrate growth and thereafter.

2. Experimental apparatus and procedure

2.1. Apparatus

As shown on Fig. 1, the current experimental setup consists of an isothermal/isobaric semi-batch stirred tank crystallizer, a gas supply reservoir for hydrate formation and a digital gasometer (*Chandler Engineering*) to measure the volume of gas expanded from the liquid sample bomb. Hydrates are formed in the 600 cm^3 internal volume stainless steel (316) crystallizer with a 12000 kPa pressure rating. A *PPI DYNA/MAG MM-006* mixer (0–2500 rpm) has been mounted on top of the crystallizer to ensure sufficient mixing. Gas is supplied from the stainless steel reservoir (internal volume of 1000 cm^3) using a *Baumann 51000 Series Low Flow* control valve. Both the crystallizer and the reservoir are submerged in a cooling bath composed of 10% glycol and water mixture controlled via a *Thermo NESLAB RTE Series* refrigerated bath. Temperature and pressure measurements are performed using standard resistance temperature devices ($\pm 0.3\,^{\circ}C$) and *Rosemount 3051S Series* pressure transducers with a reference accuracy of 0.04% of the span. The readouts are then recorded and displayed using the *National Instruments NI-DAQ 7* data acquisition device and the *LabVIEW* software. The *LabVIEW* interface was written to calculate the number of moles consumed at any time during the experiment using the Trebble–Bishnoi equation of state [22], the gas reservoir pressure and temperature measurements, as well as the gas reservoir volume. The standard uncertainties were estimated to be $u_T = 0.3$ K, $u_P = 5.6$ kPa, $u_{gasometer} = 1$ ml and $u_{bomb} = 0.2$ ml, for temperature, pressure, gasometer and sample bomb respectively.

2.2. Procedure

Prior to any experiment, the crystallizer is cleaned using HPLC grade water and purged several times using the selected gas (carbon