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Reaction rate constant of propane hydrate formation

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Abstract

Experimental data on the rate of formation of propane hydrates were obtained using a particle size analyzer capable of detecting particles with diameters as small as 0.6 nm, while operating in a closed loop system. Experiments were carried out at temperatures around 274 K and pressures between 315 and 340 kPa in a semi-batch stirred tank crystallizer. The experimental data were analyzed using a newly developed kinetic model based on crystallization theory and as a result, the actual reaction rate constant for propane hydrate formation was successfully determined. A value of 2.15×10^{-7} m/s is reported at 274.2 K, while it was found that the dissolution rate of propane at the vapor–liquid water interface was enhanced by a factor of five during the growth stage, compared to the value obtained during typical solubility experiments.

Keywords: Gas hydrate; Kinetics; Reaction rate constant; Particle size analysis; Crystallization

1. Introduction

Gas hydrates are crystalline solids that form when 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 hydrate forming gas molecule stabilizes the water lattice through physical bonding via weak van der Waals forces. Up to now, three hydrate structures have been reported in the literature, including structure I (sI), structure II (sII) and structure H (sH). 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 methane hydrates as an alternate energy source, storage and transportation of natural gas hydrates or liquefied pretroleum gases and carbon dioxide sequestration. Such promising new technologies are reasons why kinetics studies should be further investigated. In particular, accurate determination of the reaction rate constant of hydrate formation is required for proper reactor design, as it is the only parameter affecting any reactor throughput and conversion that remains constant upon scale-up, while both heat transfer and mass transfer effects will vary. Fig. 1 below shows the three-phase equilibrium line for the propane–water system using the experimental data of Deaton and Frost [1], where hydrate, liquid water and vapor are at equilibrium (H–Lw–V). Above the three-phase line, hydrate–liquid water is present (H–Lw), while below the line, vapor–liquid water is present (V–Lw).

A typical mole consumption plot for a hydrate kinetic experiment is shown in Fig. 2. The first stage is the dissolution stage where gas dissolves into the bulk liquid phase up to its equilibrium value, at the experimental temperature and pressure. Any further dissolution leads to a supersaturated solution where hydrate nuclei can form and decompose until they reach a critical nuclei diameter. This subsequent step is denoted as the nucleation stage. Once the turbidity point is reached, that is when the mole consumption deviates from its constant value reached at the end of the nucleation stage, the growth stage is initiated.

Various studies have been conducted to determine the reaction rate constant of gas hydrates. Englezos et al. [2,3] performed experiments using methane and ethane hydrates without any particle size distribution measurement. They used an average linear growth based on a population balance and assumed homogeneous nucleation. Malegaonkar et al. [4] repeated the same procedure (no particle size distribution measurement) and assumptions made previously by Englezos et al., but for methane and carbon dioxide hydrates. More recently, Clarke and Bishnoi have performed experiments to determine the intrinsic reaction

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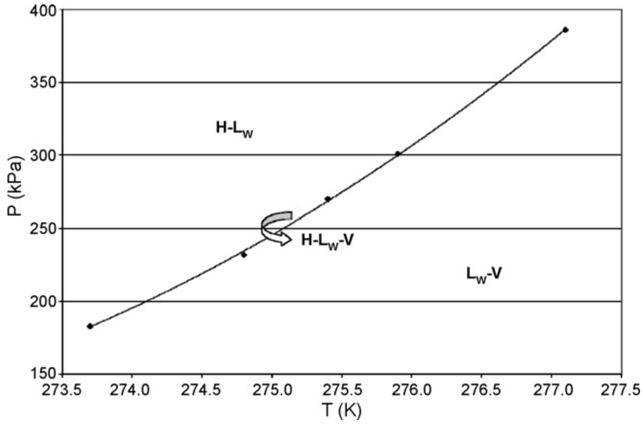

Fig. 1. Propane–water phase diagram using the experimental data of Deaton and Frost [1].

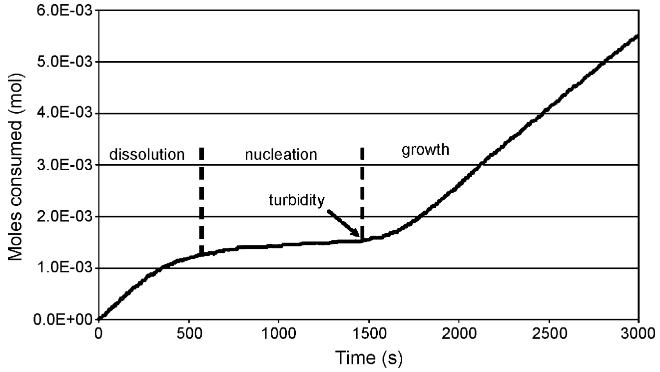

Fig. 2. Mole consumption plot at 274.2 K and 340.4 kPa (P_{eq} = 204.6 kPa).

rate constant for various hydrate systems [5–10]. Throughout their work, they used ex-situ and in-situ particle size analyzers to obtain the particle size distribution of both carbon dioxide and ethane gas hydrates, as well as mixtures of methane and ethane hydrates. The apparatus used allowed them to measure particles with chord lengths as small as 0.5 μm. Due to instrument limitations, they had to extrapolate their particle size distributions for diameters smaller than 0.5 μm. In addition, their analysis assumed homogeneous nucleation. Recently, Hashemi et al. [11] have highlighted some points that need to be addressed concerning the determination of the intrinsic reaction rate constant of hydrate formation.

The current work proposes a newly developed kinetic model based on the work of Englezos et al. [2,3], as well as a novel experimental setup to accurately measure the true reaction rate constant for propane hydrate formation. This work can be readily expanded to other hydrate systems, including methane and carbon dioxide gas hydrates.

2. Experimental apparatus and procedure

2.1. Apparatus

As shown in Fig. 3, the current experimental setup consists of an isothermal/isobaric semi-batch stirred tank crystallizer, a gas supply reservoir for hydrate formation and a *Zetasizer Nano ZS* particle size analyzer (*Malvern Instruments*). Hydrates are formed in the 600 cm^3 internal volume stainless steel crystallizer (12,000 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 300 cm^3) using a *Baumann 51000 Series Low Flow* control valve. Both the crystallizer and the reservoir are submerged in a cooling bath controlled via a *Thermo NESLAB RTE Series* refrigerated bath. The liquid phase is continuously circulated through a flow cell with a 500 kPa pressure rating (*Hellma*) in the *Zetasizer Nano ZS* particle size analyzer by means of a *LabAlliance Model 1500* dual piston pump. The *Zetasizer Nano ZS* particle size analyzer is capable of detecting particles with diameters ranging from 0.6 nm to 6 μm, with an uncertainty of 0.4% on the size obtained from the intensity distribution. In addition, it has an internal cooling system. Temperature and pressure measurements are performed using standard resistance temperature devices (±0.3 K) and R*osemount 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 of gas in the hydrate phase at any time during the experiment using the Trebble–Bishnoi equation of state [12], with an uncertainty of 1.0×10^{-4} mol.

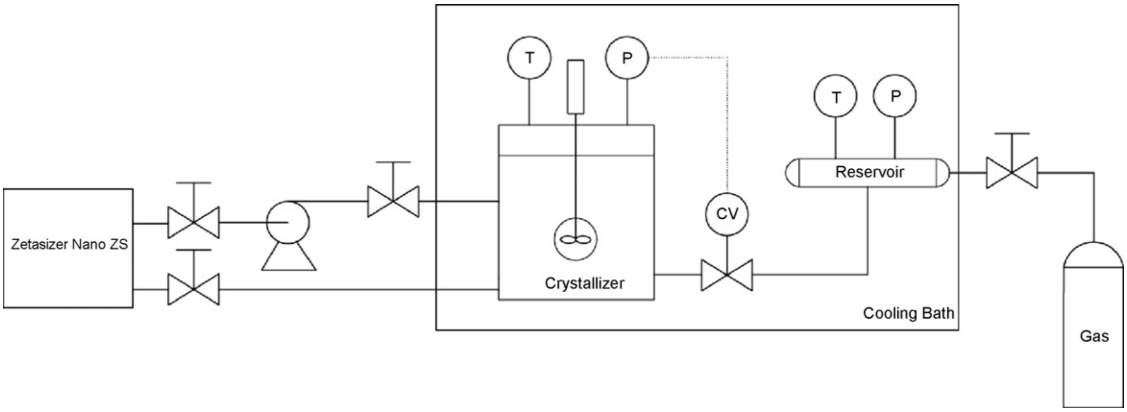

Fig. 3. Simplified schematic of the experimental setup.