Formation kinetics of cyclopentane–methane binary clathrate hydrate

CrossMark

Lichao Cai, Brian A. Pethica, Pablo G. Debenedetti, Sankaran Sundaresan *

Princeton University, Department of Chemical and Biological Engineering, NJ 08544, USA

HIGHLIGHTS

- Formation rate of cyclopentane–methane hydrate is measured in fresh water.
- Methane occupancies are estimated at different operating conditions.
- Identified methane mass transfer as a rate limiting step.

ABSTRACT

Clathrate hydrates with two guest species fitting different-sized cages can form at warm temperatures and/or low pressures, and this extended range of thermodynamic stability is favorable to many hydrate based applications. In the present study, the kinetics of formation and growth of cyclopentane–methane hydrate is studied at several temperatures ($T > 288$ K) and pressures ($P < 3$ MPa), where neither single-guest methane hydrate nor single-guest cyclopentane hydrate forms. Experiments were performed in a well-stirred vessel with water being available in excess of stoichiometric amount. Using the measured temperature and pressure trajectories, the temporal evolution of hydrate formation rate is deduced. As one would expect, the amount of hydrate formed in a prescribed time increases with the degree of subcooling. The rate of hydrate formation is shown to be limited by the rate of methane mass transfer.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Clathrate hydrates are ice-like crystalline solids with guest species occupying cages of various sizes, formed by hydrogen-bonded water molecules. The clathrated guest species, ranging from small molecules such as H_2, N_2, Xe and CH_4 to relatively large molecules such as isobutane and cyclopentane (CP), stabilize the hydrate structure and allow its formation above the normal freezing point of water (273 K). First discovered by Davy (1811), clathrate hydrates long remained a scientific curiosity and attracted considerable attention only after being found responsible for pipeline obstructions in oil production (Sloan and Koh, 2007). Hydrate formation is potentially beneficial in other instances, however, such as natural gas storage (Gudmundsson et al., 1998; Thomas and Dawe, 2003; Khokhar et al., 1998; Kumar et al., 2008; Sloan, 2003), CO_2 capture and sequestration (Yamasaki et al., 2000; Saji et al., 1992; Mondal et al., 2012; Ho et al., 2013; Babu et al., 2013; Lee et al., 2010; Linga et al., 2007a), gas separation (Kamata et al., 2005; Lee et al., 2009; Cha et al., 2010), H_2 storage

(Florusse et al., 2004; Strobel et al., 2006; Lee, H. et al., 2005; Anderson et al., 2007) and desalination (Bradshaw et al., 2007; McCormack and Niblock, 1998, 2000; Cha and Seol, 2013; Park et al., 2011; Mccormack and Ripmeester, 2013), which encourages further studies on the thermodynamic stability and formation rates of hydrates so that economically viable hydrate-based processes could be developed.

Methane hydrate has been examined as a vehicle for storage and transportation of methane (Gudmundsson et al., 1998; Kim et al., 2010), and the hydrates of butane, CCl_2F_2 (Miller, 2003) and R141b (CH_3CCl_2F) have been considered for desalination (Bradshaw et al., 2007; McCormack and Niblock, 1998, 2000). However, these single-component hydrates require either high pressures or low temperatures to form, and the cost of pressurization and/or refrigeration detracts from their economic viability. In the present study, we consider the use of binary hydrates as a potential means of achieving operation under more favorable pressure and temperature conditions. By filling the large cavities of an sII (Sloan and Koh, 2007) hydrate with a primary hydrate former (sometimes referred to as large molecule guest substance, Tsuji et al., 2004; Lee et al. 2005a,b) such as cyclopentane (CP), and the small cavities with a helper gas such as CH_4, stability is enhanced, allowing hydrate production at much lower pressures
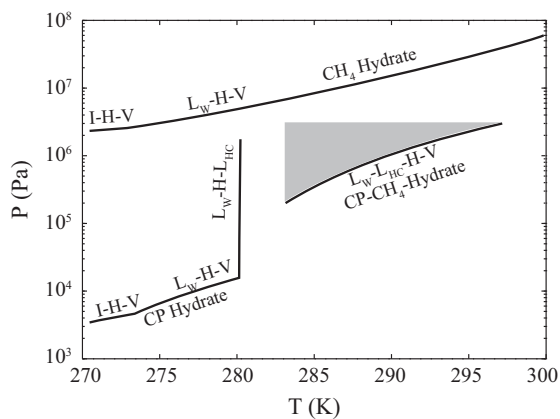
Fig. 1. Hydrate equilibrium conditions for (a) CH₄ hydrate (curve fitted from data reported in Sloan and Koh, 2007); (b) CP hydrate (curved fitted from Tohidi et al., 1997); (c) CP–CH₄ hydrate (curved fitted from data in Sun et al., 2002; Tohidi et al., 1997 as well as our measurements). The shaded area represents our preferred operating window. I: ice; H: hydrate; V: vapor; L_w: water-rich liquid; L_{HC}: hydrocarbon-rich liquid (CP).

Table 1
Four-phase equilibrium temperatures for several binary hydrates.

	Four phase equilibrium temperature (K)	
	1.0 MPa	2.0 MPa
CP–CH₄ hydrate (Tohidi et al., 1997)	290	294
CP–Kr hydrate (Takeya and Ohmura, 2006)	295	300
FCP–Kr hydrate (Imai et al., 2006)	298	302
CP–CH₃F hydrate (Takeya et al., 2008)	301	304
FCP–CH₃F hydrate (Takeya et al., 2008)	303	306
CP–CH₂F₂ hydrate (Imai et al., 2005)	297	–
FCP–CH₂F₂ hydrate (Imai et al., 2006)	299	–
CP–CO₂ hydrate (Zhang and Lee, 2009)	287	291

(than are possible with only the helper gas) and higher temperatures (than are possible with only the primary hydrate former). The resulting elimination of energy-intensive refrigeration or compression to high pressures could lead to economically more viable processes.

Fig. 1 illustrates this concept. Hydrate equilibrium curves above which the hydrates are thermodynamically stable are displayed for three different hydrates taken from literature data (Sloan and Koh, 2007; Thakore and Holder, 1987; Fan et al., 2001; Tohidi et al., 1997; Sun et al., 2002) and are in agreement with measurements obtained as a part of the present study. Methane, a common small hydrate former, forms a type sI hydrate over a wide temperature range, at least as high as 320 K (Nakano et al., 1999), but requires very high pressures (e.g. > 13 MPa for 15 °C and above). Cyclopentane, a typical heavy guest species, occupies the large cages of a type sII hydrate; its hydrate formed from fresh water can be stable at mild pressures but only below its quadruple point temperature with water (280.2 K, Fan et al., 2001) and refrigeration will usually be necessary to form CP-hydrates from salt water. CP–CH₄ hydrate, however, can form at warmer temperatures and modest pressures, where the corresponding single-component hydrates do not form. For example, at 2 MPa, CP–CH₄ hydrate can remain stable at temperatures as high as 294 K; this means that, by forming this hydrate with sufficient CP/CH₄, up to 20% of water initially at 277 K can be converted into hydrates without any heat removal (with the heat released upon hydrate formation simply warming the system from 277 K to 294 K).[1]

One can form hydrates at even more favorable conditions by using more efficient primary hydrate formers (such as fluorocyclopentane, FCP) and helper gases (such as CH₃F, CH₂F₂ and Kr). Another common helper gas, CO₂, could also be employed, albeit the corresponding binary hydrates form at less ambient conditions. The four-phase hydrate equilibrium temperatures for several different hydrate formers and helper gas combinations at two different pressures are summarized in Table 1. Thus, from a thermodynamic perspective, there are many potential binary hydrate candidates for hydrate-based desalination.

Single-component hydrates containing hydrate formers that are sparingly soluble in water typically form at or in the vicinity of the phase interface, and the growth could become limited by

transport across the growing hydrate layer (Sloan and Koh, 2007). Transport resistance may be of even greater concern in the formation of binary hydrates. In order to maximize the benefits afforded by binary hydrates, they must be formed at conditions outside the stable regions of the corresponding single-component hydrates, ensuring that the binary hydrates will grow only when water, primary hydrate former and the helper gas are all available. For instance, in the formation of CP–CH₄ hydrates, four phases are involved – an aqueous phase, hydrate, CP-rich liquid and CH₄-rich vapor. With hydrate growth mostly occurring at or near the surface of CP droplets dispersed in water, the mass transfer of CH₄ to the growing hydrate could become a rate-limiting step.

If binary hydrates form much more slowly than single component hydrates, then they would prove to be impractical for processes such as desalination even if they are attractive from thermodynamic viewpoint. Therefore, it is important to compare the typical rates of formation of single-component and binary hydrates. A few studies have explored the kinetics of hydrates formed with gaseous former mixtures (Englezos et al., 1987; Linga et al., 2007b; Kini et al., 2004) and THF-based binary hydrates (Linga et al., 2007b; Luo et al., 2006; Nagai et al., 2008), but the kinetics of binary hydrates involving a water-immiscible liquid former plus a helper gas have not received much attention in the literature. Some studies employed a second guest species as a kinetic promoter (Partoon and Javanmardi, 2013), but its role is merely auxiliary to the production of single-component hydrates. In a recent study, CP–CH₄ hydrate was produced in a 40 L bubble column reactor (Lv et al., 2012) and the methane uptake was quantified; however, water conversion is not known since the occupancy was not determined, and at the low temperatures employed in the experiments (< 280 K) both CP hydrate and CP–CH₄ hydrate could form.

The present study, which is a part of a larger effort exploring of the viability of binary hydrate-based desalination, examines the kinetics of hydrate formation in water–CP–CH₄ systems. Although one should study the kinetics of hydrate growth in saline water to fully assess the process viability, the present work focuses on hydrate formation in fresh water, as it would serve as an upper bound on achievable rates. We specifically seek to estimate water conversion rates and methane occupancy levels in CP–CH₄ hydrates under conditions where only binary hydrates can form. The study is limited to conditions where the aqueous phase is in excess.

2. Experimental setup

Fig. 2 shows a schematic of the experimental setup used in this study, which includes a 450-mL stainless steel reactor (Parr 4567), a Pt100 Resistance Temperature Detector (RTD) probe (Class 1/10 DIN, OMEGA Eng. Inc., accuracy ~ ± 0.04 °C between 0 and 20 °C) and a pressure transducer (Viatran 345, accuracy of 0.6% of the full

---

[1] Ignoring the heat capacity associated with the hydrate formers and assuming that the hydrate's melting heat per mole of water is close to that of ice.