

Formation of cyclopentane methane binary clathrate hydrate in brine solutions



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HIGHLIGHTS

- Formation rate of cyclopentane–methane hydrate is measured in brine solutions.
- Methane occupancies are estimated at different operating conditions.
- Evaluated the hydrate growth rate reduction caused by salt.

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ABSTRACT

Building on our previous study on the kinetics of formation of cyclopentane (CP)–methane binary sII-type hydrate in well-agitated fresh water, analogous experiments have been performed in brine solutions at two salinities (3.5% and 7.0% NaCl, w/w) to investigate how salt affects this formation process thermodynamically and kinetically. The hydrate formation rate in salt water is found to be ~2–3 times smaller than that in fresh water at small subcooling levels $\Delta T < 4$ K but at higher subcooling levels, the two become comparable. The methane occupancy in the small cavities of the sII hydrate is also estimated to be ~0.5 for methane pressures between 1 and 3 MPa under equilibrium conditions, as well as during growth at subcooled conditions ($\Delta T < \sim 7$ K).

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1. Introduction

A wide range of guest species methane, ethane, carbon dioxide etc. form clathrate hydrates of various structures (sI, sII, and sH) with water (Sloan and Koh, 2007). Clathrate hydrates feature cages of various sizes formed by water molecules connected via hydrogen bonding. These cages are partially occupied by guest molecules that stabilize the structure, allowing hydrates to remain thermodynamically stable (often at elevated pressures) over a range of temperatures well above the ice melting point. Hydrates in oil pipelines can lead to flow assurance problems that motivated early extensive study to better understand and suppress their formation (Sloan and Koh, 2007; Sloan et al., 2011). More recently, clathrate hydrates have been proposed in several applications, including natural gas storage/transportation (Gudmundsson et al., 1998; Thomas and Dawe, 2003; Khokhar et al., 1998; Kumar et al., 2008; Sloan, 2003), carbon dioxide capture and sequestration (Yamasaki et al., 2000; Saji et al., 1992; Mondal et al., 2012; Ho

et al., 2013; Lee et al., 2010; Babu et al., 2013; Linga et al., 2007, 2007; Babu et al., 2015) and desalination (Bradshaw et al., 2007; McCormack and Niblock, 1998, 2000; McCormack and Ripmeester, 2014; Cha and Seol, 2013; Cai et al., 2014; Park et al., 2011; Kang and Linga, 2014; Han et al., 2014), and several of them could benefit from hydrate being produced at higher temperatures and/or lower pressures. A continuous hydrate-based desalination process would involve a crystallizer in which brine or seawater is mixed with appropriate hydrate formers – usually at sea surface level or at depth to take advantage of greater pressures (Max, 2003), washing unit (Wiegandt et al., 1972, 1978; McCormack and Niblock, 1998, 2000; Han et al., 2014) to separate the salt-free hydrate particles from concentrated brine solutions, and a device to melt the hydrate to produce fresh water and recover hydrate former(s) as well as a small amount of seed hydrate crystals to be returned to the crystallizer. These could be configured for both continuous and semi-continuous operation. The formation of hydrate is usually favored by lower temperatures and higher pressures; single component hydrates, as discussed in our earlier study (Cai et al., 2014), usually require either high pressures (such as methane hydrate) or low temperatures (such as cyclopentane hydrate and $\text{CH}_3\text{CCl}_2\text{F}$ hydrate), and the cost of refrigeration and/or

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pressurization is unfavorable to hydrate-based desalination. The use of binary hydrate could be a potential solution to reduce such cost significantly.

With their large and small cavities filled with different guest species of appropriate sizes, binary clathrate hydrates can form at combinations of higher temperatures and lower pressures, where neither of the corresponding single component hydrates is stable. Cyclopentane (CP)–methane binary hydrate, thermodynamically stable up to 22 °C at a moderately elevated pressure of 2 MPa, conditions where neither methane nor CP hydrates is stable, is a typical candidate for desalination processes. However, the kinetics of its formation are less well understood. With four phases involved – a CH₄-rich vapor phase, a hydrocarbon-rich liquid, an aqueous phase and the hydrate solid phase – the formation and growth of this hydrate is likely to occur at the interfaces between the latter three. This suggests two possible mass transfer barriers:

1. Methane must be transferred from the vapor phase into and across one or both liquid phases to reach the vicinity of the hydrate growing sites.
2. If the aqueous phase is saline, the salt rejected upon hydrate formation must diffuse away. Its accumulation in the vicinity of the growing solid hydrate could lower the driving force for hydrate growth, the so-called concentration polarization effect.

In our previous paper (Cai et al., 2014) the kinetics of the CP–methane binary hydrate growth with fresh water were studied in a well-stirred vessel, and analyzed to show that (CH₄) transfer largely defines the overall hydrate growth rate, and that facilitating CH₄ transfer would promote the hydrate growth rate. In order to assess the viability of hydrate-based applications such as desalination, which involve forming mixed hydrates from saline water, one must also quantify the effect of salt on hydrate growth rate. With this in mind, the present study examines the kinetics of formation of CP–CH₄ hydrates in saline water. Salt dissolved in the aqueous phase will affect both thermodynamic and kinetic aspects of hydrate growth:

1. Thermodynamically, the introduction of dissolved salt lowers the chemical potential of water in the aqueous phase, making it less favorable to form the hydrate. As a result, a lower temperature (*T*) and/or a higher pressure (*P*) for the helper gas is needed to form the hydrate. In this study, the hydrate equilibrium temperatures corresponding to various methane pressures are measured at salinities of 3.5% and 7% (NaCl, w/w).
2. Kinetically, as noted above, the concentration polarization effect associated with NaCl rejection by the growing hydrates may limit the hydrate formation rate, even if hydrate formation in saline is allowed to occur at the same subcooling level as in the fresh water case. In this study, hydrate formation kinetics are measured over a range of *T*, *P* and salinities to assess the severity of concentration polarization.

2. Experimental setup

The equipment and schematics employed in this work are the same as in our previous study (Cai et al., 2014). Briefly, the hydrates are formed in a 450 mL stainless steel reactor equipped with an annular jacket through which a coolant is circulated. The coolant temperature is controlled by a Julabo thermostat. Multiple ports on the reactor head allow injection/discharge of selected hydrate formers (gas/liquid); a Resistance Temperature Detector (RTD) probe (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 full range 0–4 MPa) are also installed and

connected to multi-meters (Agilent 34410A) to allow continuous *T* and *P* measurements. Mechanical stirring is achieved via a magnetic drive without a rotating seal. The controllers/detectors for *T*, *P* and stirrer speed are managed by a LabVIEW program, which performs a series of pre-scripted experiments in a reliable and reproducible fashion. Additional details can be found in our earlier article (Cai et al., 2014).

2.1. Procedure for measuring hydrate equilibrium conditions

The hydrate equilibrium conditions are determined experimentally by monitoring their formation/dissociation (Sloan and Koh, 2007), which is sometimes achieved through visual observation (Deaton et al., 1946) or using more sensitive apparatus such as a Quartz Crystal Microbalance (Mohammadi et al., 2003). As the vessel used in our experiments is not transparent, we followed an isochoric procedure based on monitoring *P* while varying *T*, which is analogous to that used by Ouar et al. (1992). The reactor is first loaded with water or brine solution and liquid CP; after purging the air in the headspace, the helper gas CH₄ is introduced up to the desired *P*. Starting from a temperature above the melting point (which is dictated by the selected *P*), the mixture is cooled down stepwise with very slow stirring, allowing a fixed time interval (30 min) following each step. The pressure at the end of each step is recorded (see the blue points in Fig. 1); the modest decline in *P* with decreasing *T* seen in the figure reflects isochoric cooling of the vapor and higher methane solubility at lower *T*. One could easily reach up to ~2 K below the melting point without forming hydrates, as both subcooling and active stirring are typically needed to trigger primary nucleation in our experiments. Next, a much lower coolant *T* is used, and intense agitation (600 RPM) is applied, in order to trigger hydrate formation, signaled by a sharp pressure drop, before raising the temperature back to ~2 K below the melting point. Since part of methane is now clathrated, the pressure is significantly lower than that observed in the cooling process at the same *T*. In the melting sequence, represented by the red points in Fig. 1, *T* is raised stepwise with a fixed time interval (120 min) between steps, and the ending pressures are recorded as shown in Fig. 1. Before the system temperature reaches the melting point, each temperature rise results in partial melting of the existing hydrate, which releases methane into the headspace.

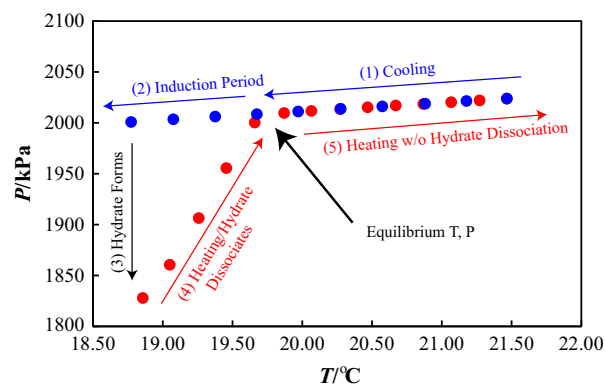


Fig. 1. Determination of CP–CH₄ hydrate four-phase equilibrium. Stage (1): the mixture is cooled down stepwise with very slow stirring, allowing a fixed time interval (30 min) following each step; the final system pressure is then recorded. Stage (2): the mixture could be cooled a few degrees below the equilibrium conditions without forming hydrates because of kinetic limitations. Stage (3): hydrate formation consumes methane and leads to substantial pressure decline. Stage (4): the mixture is heated stepwise while maintaining intense stirring, allowing a fixed time interval (120 min) following each step; the system pressure is then recorded. Stage (5): heating hydrate-free mixture in steps above the melting point. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)

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