



Preservation of methane gas in the form of hydrates: Use of mixed hydrates



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ABSTRACT

The release of methane gas was compared in pure CH₄ (sl) and mixed (sII) hydrates (with C₄H₈O – tetrahydrofuran and C₃H₈ – propane) having methane as dominant constituent. We report absence of the self preservation effect in mixed hydrates, having stoichiometric composition (sII) of larger guest molecules, and they populate the 5¹²6⁴ cages. Their dissociation behaviour is in accordance with the respective phase boundary curve. While a partial methane gas release was observed at 270 K, particularly, in dilute systems. Further, excess gas release was at T > 270 K and complete methane release is governed by the thermodynamic stability of mixed hydrates.

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1. Introduction

Adaptability of gas hydrate based technology for natural gas storage and transportation demands a stringent pressure and temperature conditions for its stability. Its transportation through a network of pipelines is particularly useful for long haul, while it becomes uneconomical for mid or short distances (Gudmundson and Borrehaug, 1996). The liquefied natural gas (LNG) or compressed natural gas (CNG) transportation methods, although, preferentially used in these sectors have inherent operational difficulties, such as need of cryo-temperature and high pressures respectively (Thomas and Dawe, 2003). Thus, these techniques require skilled man-power for sustained and safer operations. Adoption of gas hydrate based methodology in this sector is attractive, but the limitations are mostly technology driven (Nakoryakov and Misyura, 2013; Mimachi et al., 2014). The hydrate conversion is quite inefficient and time consuming without an agitator and therefore some special reactors are being employed. Another approach is to add of some kinetic promoters or surfactants to the hydrate forming (gas + water) system; and such experiments are still at laboratory scale (Ganji et al., 2007).

Additionally, usage of certain porous materials have shown some attractive features in hydrate conversion process (Prasad et al., 2014; Chari et al., 2013a, b; Kang et al., 2010, 2013; Linga et al., 2007).

Clathrate hydrates, or gas hydrates, are the crystalline ice-like inclusion compounds consisting of hydrogen bonded water molecules forming open cages of different sizes. Four essential conditions often required for its stable existence are (i) enough supply of guest (suitably sized hydrocarbons or other) and (ii) host (water) molecules; and simultaneous presence of (iii) moderately high pressure, (iv) lower temperature conditions. Such stringent requirements are often fulfilled in certain geological locations around the globe, both under the permafrost and the oceanic sediments. Typical pressure and temperatures for the methane hydrates stability are 2.5 MPa and 273 K; and required pressure increases exponentially at higher temperatures (Sloan and Koh, 2008). On the other hand gas hydrates encasing methane molecules (dominant constituent in natural gas hydrates) can be preserved for a longer duration even at ambient pressure in the temperature window 240–270 K, and this is most popularly known as “anomalous (or self-) preservation effect” (Stern et al., 2001, 2003). The metastable nature of methane hydrates (MH) has been a subject of immense interest; however, a precise molecular mechanism responsible for this effect has not emerged. For example, is it an exclusive property

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for methane hydrates (sl - *Pm3n*) alone or is it true for all other sl or sII (*Fd3m*) hydrates also. Will the mixed hydrates (sII), with CH₄ as dominant fraction, possess this exceptional property? How can one model the mechanism for this unique property without ambiguities? Nevertheless unexpected longevity of the methane hydrates at ambient pressure found important applications, particularly, in gas storage and transportation of natural gas hydrates, which are dominated by the methane gas (Takeya et al., 2012; Mimachi et al., 2014). There are several factors that control the rate of hydrate dissociation, such as experimental temperature (Stern et al., 2001, 2003) and pressure (Komai et al., 2004). Further, composition of the feed gas (Stern et al., 2003; Takeya and Ripmeester, 2010; Uchida et al., 2011), hydrate granular size (Takeya et al., 2005; Mimachi et al., 2014) and co-existence of certain additives or electrolytes (Zhang and Rogers, 2008; Takeya et al., 2012; Sato et al., 2013), and presence of fine glass beads (Hachikubo et al., 2011) in hydrate forming systems also influence the dissociation process. The effect of temperature on the dissociation process is exhaustively studied in the past by Stern et al. (2001) and they reported significantly slower at atmospheric pressure in a temperature window 241–271 K (generally known as self-preservation window), with two minima at 249 and 269 K. Nakoryakov and Misyura (2013) have reported that the thermal dissociation rate is significantly lower in natural hydrates compare to synthetic analogues in self preservation window despite of structural similarity.

Takeya and Ripmeester (2010) have shown that the self-preservation property is not an exclusive for MH alone, but the hydrates with certain other guest molecules like CH₃F, CF₄ and CO₂ forming sl structure and O₂, N₂, Ar and Kr forming sII can also show this phenomenon. These authors further argued that the interactions between the guest molecules and H₂O molecules in ice play a critical role in self-preservation phenomenon. Uchida et al. (2011a, b) have summarized earlier kinetic models on this unusual self-preservation phenomena and have concluded that the ice shield, around hydrate grains, below 240 K is mostly granular type and the retardation in gas diffusion is governed by slower hydrate dissociation rather than gas diffusion. However, in the self-preservation temperature region, *i.e.*, 240 K < T < 270 K, the morphology of ice shield is plate-like with stacking faults and hydrate dissociation is governed by the molecular gas diffusion through the ice layers. Further, the ice layer also stabilizes the hydrate structure vindicating the importance of gas-H₂O interactions in this phenomenon. Takeya et al. (2011) have measured the average thickness of ice layer around hydrate particles as 100 μm after preserving them for 24 h at 253 K. Although it is difficult to understand the effect of gas-H₂O interactions on the self-preservation of gas hydrates quantitatively, they become very important when we consider the natural gas hydrates as storage and transportation materials. Zhang and Rogers (2008) claimed that the 0.04% of the stored gas was evolved during 256 h at 268 K from the hydrates formed with gas mixture of (CH₄ + C₂H₆ + C₃H₈) at atmospheric pressure. According to these authors, ice shielding is not the primary mechanism for this phenomena and the enhancement of preservation by usage of additives may be of practical possibility. Recently Kida et al. (2011) proposed that the “direct measurements of the dissociation behaviours of pure methane and ethane hydrates trapped in sintered tetrahydrofuran hydrate through a temperature ramping method showed that the tetrahydrofuran hydrate controls dissociation of the gas hydrates under thermodynamic instability at temperatures above the melting point of ice”. The sample preparation procedure adopted by Kida et al. (2011) involved several steps, such as mixing-up of fine powders of independently prepared MH and THF hydrates at low temperatures. Later they were pelletized using oil pressure of 6 MPa and 263 K. Further prior to depressurization experiments,

the pellets were again broken into 1–2 mm chips and were soaked for about 30 min under methane gas pressure of 6 MPa and 263 K. Thus, the possibility of mixture of both sl (MH) and sII (THF + CH₄) hydrates cannot be excluded in such experiments. Thus it was not clear whether the delayed dissociation of hydrates was due to mixed hydrates or due to anomalous preservation nature of sl hydrates. In order to gain further understanding we compared the dissociation behaviour of methane hydrates (MH), after depressurization, in its pure (sl) and mixed (with THF – 0.052, 0.021 & 0.011 and C₃H₈ gas – 0.13, 0.051 & 0.017 mol fractions) form. The THF is highly soluble in water and readily form sII hydrates, while propane is less soluble and also form sII hydrates because of its larger molecular size.

2. Experimental

Experimental procedure followed for gas hydrate synthesis has already been described earlier (Chari et al., 2011, 2013a; Sharma et al., 2014). Briefly, the main part was an SS-316 cylindrical vessel, which can withstand gas pressures up to 15 MPa, and volume of the vessel was 400 mL. A cold fluid (water + glycol mixture) was circulated around the vessel with the help of a circulator to bring and maintain temperature inside the cell at a desired level. A platinum resistance thermometer (Pt100) was inserted into the vessel to measure temperature with an accuracy of ±0.5 K, while pressure in the vessel was measured with a pressure transducer (WIKA, type A-10 for pressure range 0–25 MPa with ±0.5% accuracy). De-ionized ultra-pure water (Millipore – type 1) was used, and the dissolved gases were removed by evacuation. The High pure gasses were supplied by M/S Linde India Private Ltd. The tetrahydrofuran of purity (98%) was supplied by Qualigens Fine Chemicals, India.

About 70% volume was for CH₄/C₃H₈+CH₄ gas and rest was filled with water or THF aqueous solution. The atmospheric gases in the experimental cell were diluted by purging with the gas prior to the experiments and the gas was filled to the desired level (5.0–8.0 MPa) using the Teledyne ISCO syringe pump to a pressure and temperature outside of the hydrate stability zone. Then, the reactor was isolated from the ISCO pump/gas tank by closing the gas inlet valve. Subsequently, a cold fluid from the chiller was circulated to bring down the temperature of the reactor and the hydrate formation was detected by a sharp pressure drop at a particular temperature (>275 K). The temperature and pressure were logged for every 60 s of the time interval. Insignificant head-pressure drop in the reactor observed over a longer duration indicates saturation in hydrate conversion. The reactor cell was then placed in a bath pre-cooled to 250 K for equilibration. Then the reactor was depressurized rapidly by venting the residual gas. The bath temperature was slowly increased and *p*, *T* of the reactor was recorded with 30 s interval. Similar experimental protocol has been used by Uchida et al. (2011a).

3. Results and discussion

Table 1, shows the mole fractions of feed guest molecules and the amount of gas liberated during the dissociation of gas hydrates. The gas release below 273 K is mostly due to the dissociation of sl component, while that above is because of sII hydrate dissociation. The hydration number for pure methane hydrates has been computed as 5.94 (Chari et al., 2014) and that for C₃H₈ + CH₄ mixtures is estimated from CSMGEM program (Sloan and Koh, 2008). The hydration number for THF + CH₄ hydrates was estimated using the cage occupancy reported by Seo et al. (2003). Estimated hydration numbers for the mixed guests vary in the range 7.80–6.72 depending on the feed guest composition. Typical

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