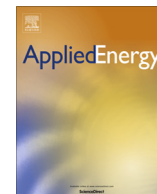




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Effect of guest gas on the mixed tetrahydrofuran hydrate kinetics in a quiescent system[☆]

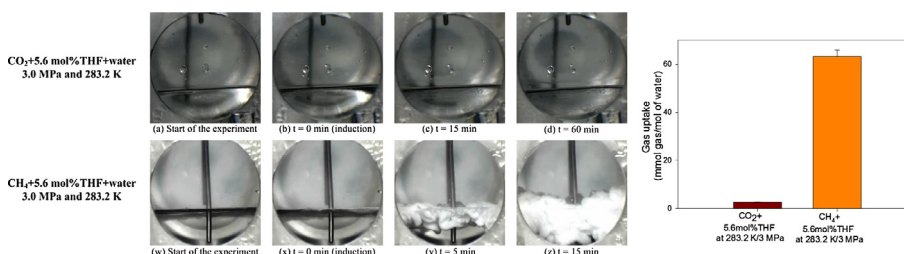
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HIGHLIGHTS

- Guest gas significantly influences the mixed tetrahydrofuran hydrate formation kinetics.
- Morphology of CO₂ hydrates in different hydrate structure domains were reported.
- Despite the higher solubility of CO₂, gas uptake observed was lower than CH₄.
- Calorimetry result presents the non-coexistence of sI and sII hydrates.

GRAPHICAL ABSTRACT



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ABSTRACT

Clathrate hydrates are ‘inclusion compounds’ that have the ability to encompass multifold volumes of guest gas molecules, thus being advantageous for gas storage and gas separation applications. CO₂ capture in the form of hydrates is an environmentally benign and cost-effective approach. In this work, we examine the kinetics of CO₂ hydrate formation at different operating conditions that result in the formation of pure sI hydrate, pure sII hydrates and/or a mixture of sI and sII hydrates. Morphology observations of different hydrates formed are presented with the associated CO₂ uptake achieved under different experimental conditions. We report strikingly contrasting morphology of mixed CO₂ and mixed CH₄ hydrates observed in presence of stoichiometric THF (5.6 mol%) under similar pressure diving force and operating conditions. Interesting results observed during mixed CO₂ hydrates using Differential Scanning Calorimetry (DSC) are documented. Based on DSC thermograms, we report interesting observations on the effect of guest gas in the mixed THF hydrate formation and dissociation. Moreover, mixed CH₄/THF hydrates were found to be more stable in comparison to mixed CO₂/THF hydrates. This work highlights that the choice of guest gas plays a significant role in the associated hydrate formation kinetics in presence of THF.

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1. Introduction

Clathrate hydrates are inclusion compounds that encompass guest molecules in host water cages. Guest molecules can be pre-

dominantly gases like methane, ethane, carbon dioxide etc., or even organic compounds like acetone, tetrahydrofuran, cyclopentane etc. Hydrates are ice-like, crystalline and non-stoichiometric compounds wherein the guest molecules are held intact only by weak Van der Waals force [1]. Due to these peculiar characteristics and other significant advantages offered including high volumetric gas storage capacity, environmental friendly nature and moderate operating conditions for formation, hydrates find applications in many areas including energy storage including methane (natural gas) [2–5] and hydrogen storage [6–8], desalination [9,10], cold storage [11,12], carbon capture and sequestration (CCS) [13–15].

[☆] The short version of the paper was presented at ICAE2016 on Oct 8–11, Beijing, China. This paper is a substantial extension of the short version of the conference paper.

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CO₂ in presence of water without any additive forms a standard sI type hydrate structure. Phase equilibrium data of CO₂ hydrates has been well documented in the literature [16–19]. Investigation of kinetics of CO₂ hydrate formation in presence of different additives has been an active research area in the last decade due the promise it offers for CO₂ capture applications. Additives can be predominantly classified into kinetic and thermodynamic promoters. Thermodynamic promoters are additives that participate in hydrate formation thereby shift/alter the pure hydrate phase equilibrium curve resulting in more moderate conditions during hydrate formation (lower pressure and higher temperature than that of pure CO₂ hydrates). Commonly studied thermodynamic additives for CO₂ hydrate formation include tetrahydrofuran (THF) [20,21], cyclopentane [22–24] and tetra alkyl ammonium salts [25,26]. Recently, Lee et al. [27] evaluated the use of neohexane, a sH hydrate forming promoter for CO₂ capture and sequestration. However, the inherent disadvantage is that these thermodynamic promoters preferentially occupy and stabilize the large sized cages of hydrate structure thereby compromising on the guest gas storage capacity. Kinetic promoters (commonly ‘surfactants’) on the other hand, alter the gas/liquid interfacial properties due to which increased hydrate formation rates are achieved. These kinetic promoters have no effect on the phase equilibrium curve, thus the addition of kinetic promoters does not result in any change in operating conditions of hydrate formation. Kumar et al. [28] studied the effect of different type of surfactants (including cationic, anionic and non-ionic) on the CO₂ hydrate formation kinetics. Mohammadi et al. [29] reported a synergism between sodium dodecyl surfactant and silver nanoparticles during CO₂ hydrate formation resulting in improved kinetics and increased CO₂ storage capacity. Apart from the application of thermodynamic and kinetic promoters, enhancement in hydrate formation kinetics could also be achieved by the employment of a fixed bed reactor that enables a higher surface area of contact between gas phase and aqueous phase. Many porous fixed bed supports like silica sand [30,31], silica gel [28,31], polyurethane foam [32], SS-316 mesh arrangements [33] and other siliceous materials like pumice and fire hardened red clay [34] have been investigated for their ability to improve the kinetics of CO₂ hydrate formation.

THF is a prominent sII hydrate structure forming guest studied as a thermodynamic promoter with different guest gases like methane [2,3], hydrogen [35,36] and CO₂ [37–39] during hydrate formation. THF is miscible with water and has the ability form hydrates without any guest gas below 4.4 °C at atmospheric pressure [35]. Torre et al. [20] investigated CO₂ hydrates formation kinetics in presence of kinetic promoter (SDS) and thermodynamic promoter (THF). The concentration of THF and SDS used were 4.0 wt% (equivalent to 1.0 mol%) and 0.3 wt% respectively. Both batch type and semi-continuous mode of operation were employed and the study was performed in quiescent reactor mode (stirred till the nucleation after which the stirrer was switched off). They report enhanced kinetics with higher water to hydrate conversions with the combination of two types of additives in comparison to the usage of individual additives and pure CO₂ hydrates (without

any additive). Lirio et al. [21] also studied the kinetics of CO₂ hydrate formation in presence of both these additives but at a higher concentration of THF(5 mol%) and lower concentration of SDS (0.05 wt%). They have studied kinetics at two different pressures of 3.0 and 5.0 MPa and two temperatures of 274.15 and 277.15 K using a stirred tank reactor configuration. Most optimal conditions for mixed hydrate formation were reported to be 3.0 MPa and 274.15 K in presence of 5.0 mol% THF and 0.05 wt% SDS. Recent study by Kim et al. [40] reports mixed CO₂/THF hydrate formation at three different concentrations of 0.5, 1.0 and 1.5 mol% THF at three different pressures of 0.5, 1.5 and 2.5 MPa. All experiments were performed at 274.15 K. Optimal conditions of hydrate formation were reported to be at 1.5 MPa using 1.5 mol% THF at 274.15 K and authors envisage the advantage of using mixed hydrate slurry for a district cooling purpose. All above listed studies report experiments that were performed under conditions that resulted in the formation of mixed CO₂/THF hydrates in regions of overlapping sI and sII hydrate domains. To our knowledge, there are no documented studies in literature examining mixed CO₂/THF hydrate formation in only sII hydrate domain. So, we chose experimental conditions for the present study to be 3.0 MPa and 283.2 K. It is not possible to form pure sI CO₂ hydrates at the chosen conditions as the equilibrium pressure of CO₂ hydrate formation at 283.2 K is 6.3 MPa [17]. Table 1 summarizes the experimental conditions employed in the current study in comparison to that of experimental conditions reported in the literature. Examination of the kinetics of mixed CO₂/THF hydrates is of practical relevance for several applications pertaining to gas hydrate technology for gas separations involving CO₂ streams like CO₂ capture from flue, fuel, land fill and bio gas streams. Further, studies by Sun et al. [41,42] examine the formation and dissociation characteristics of CO₂/THF mixed hydrates. Reduction of CO₂ emission (utilizing CO₂ during hydrate formation) coupled with the application of cold energy (during hydrate dissociation) suited for district-cooling application is envisaged through CO₂/THF mixed hydrates [40–42]. Kim et al. [40] estimated the coefficient of performance (COP) of CO₂ + THF hydrate cooling system to be 11.55.

Recently, Veluswamy et al. [3] reported enhanced methane hydrate formation kinetics in presence of THF promoter at lower pressures of 3.0 MPa and 283.2 K with high methane storage capacity in unstirred tank reactor (UTR). The objective of the current study was to evaluate if such similar enhancement of hydrate formation kinetics could be observed for CO₂ hydrates in presence of THF in UTR under similar operating conditions. Experiments were performed at same temperature and pressure. Equilibrium pressure for mixed CO₂/THF hydrates at 283.2 K is interpolated to be about 0.6 MPa [43], very close to the equilibrium pressure of 0.5 MPa for mixed CH₄/THF hydrates at 283.2 K [44] thus ensuring similar pressure driving force for the hydrate formation for both systems. Gas uptake and kinetics achieved under different hydrate structure forming experimental conditions were documented with associated morphology observations. In the current study, we also chose experimental conditions for hydrate forma-

Table 1
Operating experimental conditions of present study in comparison with literature.

Study	THF concentration (mol%)	Experimental temperature (K)	Experimental pressure (MPa)	Reactor configuration
This study	5.6	283.2 (Constant temperature)	3.0	Unstirred
This study	5.6	274.2 (Constant temperature)	3.0	Unstirred
Torre et al. [20]	1.0	Cooling from 293.2 K to 275.2 K	2.7	Stirred till nucleation followed by unstirred
Lirio et al. [21]	5.0	Cooling from 293.2 K to 277.2 K or 274.2 K	3.0 and 5.0	Stirred
Kim et al. [40]	1.0, 1.5 and 3.0	274.2 (Constant temperature)	0.5, 1.5 and 2.5	Stirred

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