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Kinetic promotion of mixed methane-THF hydrate by additives: Opportune to energy storage

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Abstract

Natural gas storage in the form of clathrate hydrates (Solidified natural gas; SNG) is an innovative and an extremely safe approach. Application of environmentally benign additives to enhance the hydrate formation kinetics is highly promising and possesses significant research potential. In this work, we elucidate the influence of hydrophilic/hydrophobic eco-friendly additives on the kinetics of mixed methane-tetrahydrofuran hydrates along with morphological observation. Further, the mixed methane-THF hydrates formed were characterized employing a high-pressure micro-differential scanning calorimetry (μ -DSC). Enhanced kinetics and microscale analysis in presence of these additives present salient information to aid the commercial deployment of SNG technology.

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Keywords: Natural gas storage; Hydrates; High pressure calorimetry; kinetics; amino acid; morphology

1. Introduction

Natural gas is a well-known, most abundantly available, cleanest and safe burning fossil/transportation fuel. However, due to low density, it is challenging to transport & store natural gas in economical and safe ways. In general, the most popular natural gas storage (in United States) is underground inventory (Depleted oil and natural gas reservoirs, aquifers, and salt cavern formations)[1]. Moreover, natural gas can be stored and transported through liquefied natural gas (LNG)/ compressed natural gas (CNG) carriers, however the cost associated in such facilities

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make them un-economical. Transportation through pipelines is also impractical across oceans and highly un-economical. In this direction, solidified natural gas (SNG) in the form of clathrate hydrates is considered as one of the most feasible options for large-scale natural gas storage/transportation [2-8]. Clathrate hydrates or gas hydrates are non-stoichiometric crystalline compounds formed by guest gas/liquid molecules and host water molecules at a suitable pressure and temperature conditions [9-11]. Over the past few decades, clathrate hydrates have also been researched for several other potential technological applications such as gas separations, carbon dioxide capture/sequestration[12-14], hydrogen storage[15] and seawater desalination[16].

Major benefits associated with SNG technology are (i) environmentally benign; (ii) high storage capacity; (iii) moderate storage conditions (iv) highly compact mode of storage; (v) extremely safe mode of storage (non-explosive nature). Despite of these benefits, there are some major challenges associated with SNG technology: (i) slow rate of hydrate formation; (ii) high pressure and low temperature requirements; and (iii) hydrate instability (sI hydrate) at moderate conditions. To overcome these challenges, we recently reported a rapid formation of mixed methane (CH_4)-Tetrahydrofuran (THF) hydrate (sII hydrate) with high thermodynamic stability. We established that THF acts as both thermodynamic as well as kinetic promoter to form hydrates quickly in a simple unstirred reactor (UTR) configuration [8, 17]. In this work, we study the influence of hydrophilic/hydrophobic environmentally benign additives (amino acids, L-Arginine and L-leucine) on the kinetics of mixed CH_4 -THF hydrate formation along with the morphological observation at moderate temperature ($\sim 20^\circ\text{C}$). Amino acids have been demonstrated as promoters for pure methane hydrate formation (sI hydrate) in few studies [18, 19] however; there is no data available in open literature for the influence of amino acid on mixed CH_4 -THF hydrate formation (sII hydrate). Moreover, employing high-pressure micro-differential scanning calorimetry (μ -DSC), we characterize the hydrates formed.

Nomenclature

THF	Tetrahydrofuran	sII	Structures II hydrate
UTR	Unstirred tank reactor	SNG	Solidified natural gas
sI	Structures I hydrate	μ -DSC	Micro-differential scanning calorimetry

2. Experimental Section

Methane gas (99.9% purity) purchased from Air Liquide Singapore Pte Ltd. was used for all experiments. Amino acids, L-arginine (reagent grade, $\geq 98\%$) and L-leucine (reagent grade, $\geq 98\%$) was purchased from Sigma-Aldrich. Tetrahydrofuran (THF) of 99.99% purity was purchased from Fisher Chemicals. Ultrapure water (from Merck Millipore) was used for all experiments.

A high-pressure micro-differential scanning calorimeter (HP μ -DSC7 from Evo, Setaram Inc.) was used in this study. The details of μ -DSC along with the experimental procedure is given elsewhere [17, 20]. Hydrate formation (kinetic) experiments were performed in an unstirred reactor (UTR) configuration. The details of the experimental setup along with the procedure is given in our previous papers [6, 21].

3. Results and Discussion

In this section, results obtained from *in-situ* analysis (Calorimeter) in small scale and the kinetic data from large-scale setup are discussed. It has to be noted that the sample size for μ -DSC analysis was 120 μL and the sample size for kinetic analysis was 32.4 mL.

3.1. Calorimetric analysis of mixed hydrates

Employing high-pressure μ -DSC, we obtained typical thermograms along with heat flow, temperature and pressure profile (Fig.1). Fig. 1a presents the multiple runs of hydrate formation and dissociation thermograms for 0.3wt% L-Arginine-water-5.56 mol% THF system at a constant pressure of 7.2 MPa and various temperatures (Run-1 at -15°C , Run-2 at -10°C , Run-3 at -5°C and Run-4 at 2°C). Fig. 1b shows the pressure profile (constant) during the DSC

runs. Fig.1c presents the extended single formation-dissociation thermograms (Run1), which was obtained using a temperature ramping program. As can be seen from the figure, during cooling step, the exothermic peak at around 0.5 h ($\sim 2^\circ\text{C}$) corresponds to the hydrate nucleation and the two endothermic peaks during heating step corresponds to the pure THF hydrate and mixed CH_4 -THF hydrates. It corroborates well with our previous study performed with water-5.56 mol% THF system without any additive [17, 20]. 5.56 mol% THF is the stoichiometric amount of THF ($\text{THF}\cdot 17\text{H}_2\text{O}$) that results in complete occupation of large cages of the resulting sII hydrate. Fig.1d shows the dissociation thermograms obtained from run-4 (temperature Vs heat flow). As can be seen in the fig.1d, hydrate nucleation occurs even during the heating step at $\sim 20^\circ\text{C}$. (It is noted that sample was cooled up to 2°C during formation/cooling step). It show cases the promotional effect of Arginine in mixed hydrate nucleation. Further, we present the hydrate dissociation thermograms (Fig.2) to compare the sI (Pure methane hydrate), sII (Pure THF hydrate) and sII (Mixed methane-THF hydrate) formed in presence of 0.3 wt% L-arginine and L-leucine at 10.0 MPa pressure and 2°C (Note: Pure THF hydrate was formed at atmospheric pressure and -10°C). Refer our previous publications for hydrate melting temperature (phase equilibria) for sI and sII hydrates presented in fig 2[6, 17, 20].

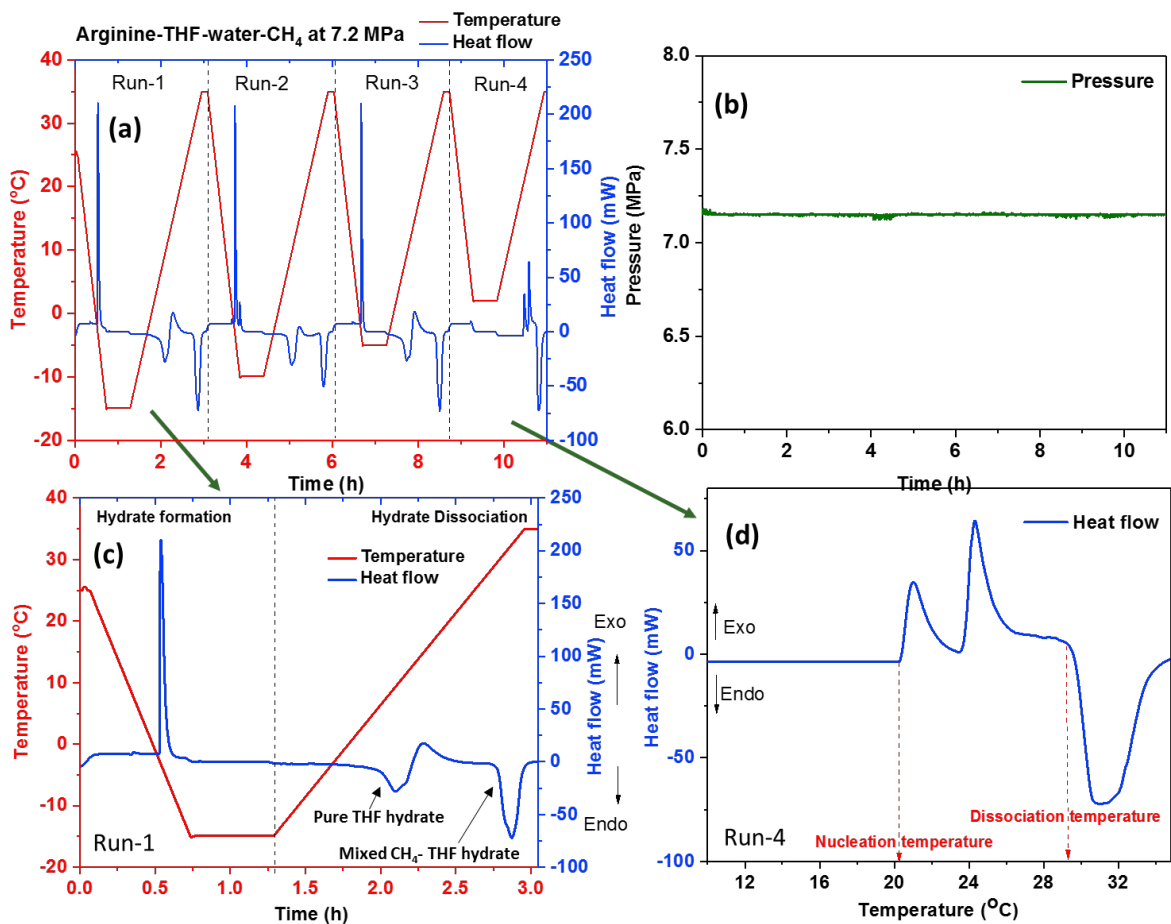


Fig.1. (a) Typical DSC thermograms of 0.3wt% L-Arginine-water-5.56 mol% THF system along with heat flow and temperature profile for hydrate formation and decomposition using a temperature ramping program, cooling from 25°C to -15°C (Run-1), -10°C (Run-2), -5°C (Run-3) and 2°C (Run-4) at $0.5^\circ\text{C}/\text{min}$ and heating to 35°C at $0.5^\circ\text{C}/\text{min}$ at 7.2 MPa pressure of methane. (b) Presents constant pressure inside the sample cell. (c) Extension for run1 and (d) extension for run4 to show the change in heat flow with respect to temperature during hydrate formation and dissociation step.

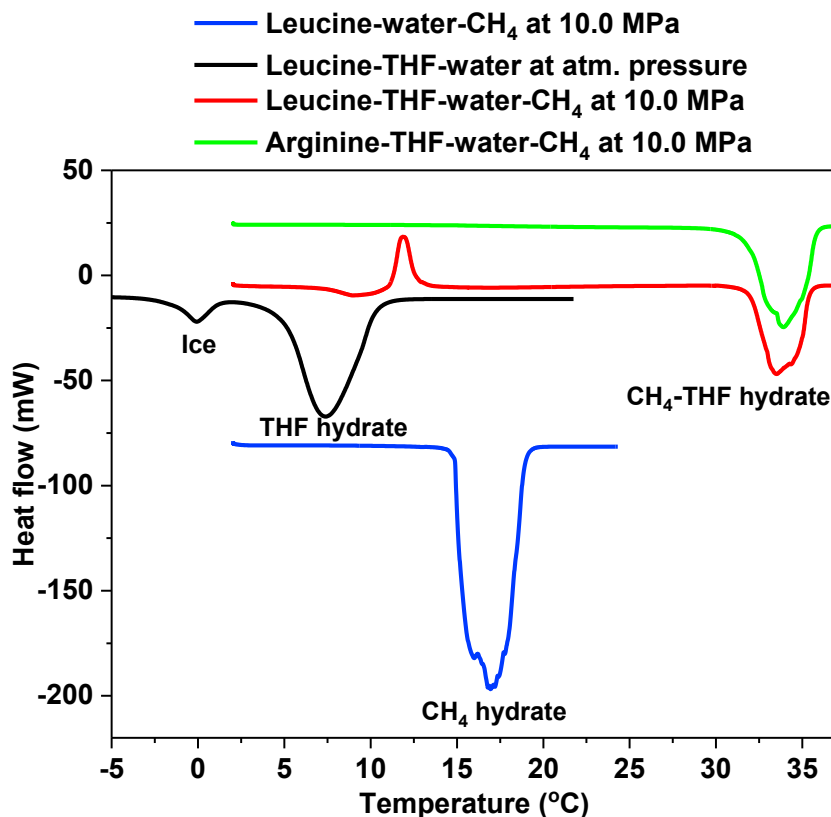


Fig. 2. Comparison of hydrate dissociation thermograms to distinguish the sI (Pure methane hydrate), sII (Pure THF hydrate) and sII (Mixed methane-THF hydrate) formed in presence of 0.3 wt% L-arginine and L-leucine in water at 10.0 MPa pressure and 2 °C (Note: Pure THF hydrate was formed at atmospheric pressure and -10 °C)

3.2. Hydrate formation kinetic analysis

Further, to understand the effect of Arginine on hydrate formation kinetics, we performed experiments in setup using 32.4 ml of sample solution. Fig. 3 compares the methane uptake profiles obtained in presence/absence of L-Arginine in water-THF (5.56 mol%) solution in an unstirred reactor configuration at 20 °C and starting pressure of 7.2 MPa. Time zero corresponds to the nucleation point. As seen in the fig.3, Arginine promotes the hydrate growth significantly. Moreover, as can be seen in the inset figure, hydrates formed in presence of L-Arginine grow in the bulk liquid phase unlike other kinetic promotes (Sodium dodecyl sulfate; SDS) in which hydrate grows along the wall of the reactor[13].

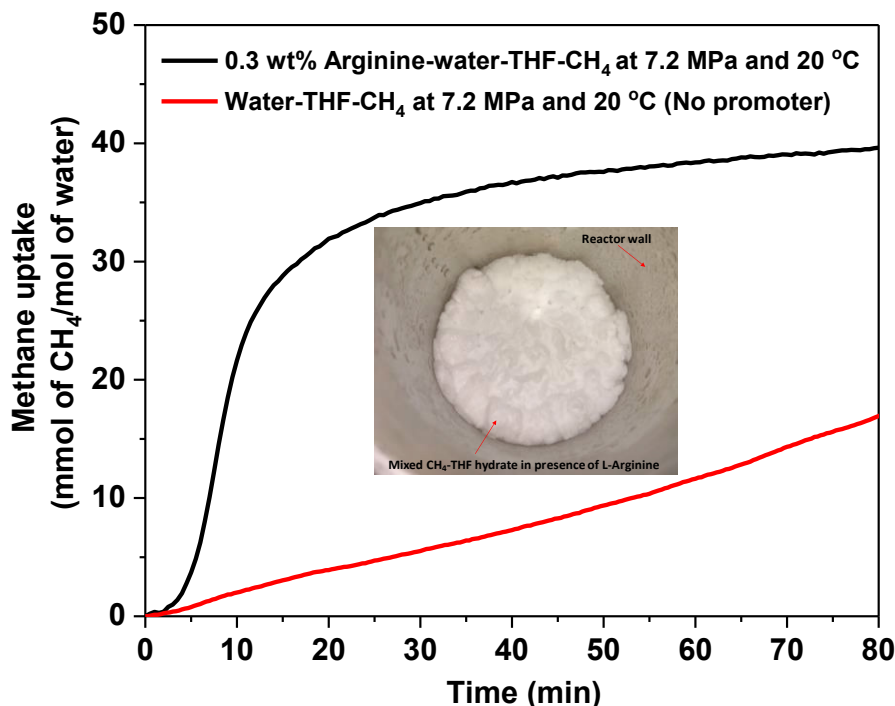


Fig. 3. Comparison of methane uptake profiles during hydrate formation experiments obtained in presence/absence of L-Arginine in water-THF (5.56 mol%) solution in an unstirred reactor configurations at 20 °C and starting pressure of 7.2 MPa. Time zero corresponds to the nucleation point. Inset figure shows the bulk hydrate formed in presence of L-Arginine.

4. Conclusions

We elucidate the effect of L-Arginine on the formation kinetics of mixed CH₄-THF hydrate at near ambient temperature condition (20 deg C). We found that Arginine promotes the hydrate growth significantly. Further, we analyze the mixed hydrates employing μ -DSC. The DSC data reveals that the presence of L-Arginine promotes the nucleation but no thermodynamic shift in the dissociation temperature is observed. Further, a detailed assay for the influence of hydrophilic/hydrophobic additives on mixed hydrate is ongoing in our laboratory.

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