

STUDYING THE KINETICS OF MIXED CH₄-THF HYDRATE FORMATION AT AMBIENT TEMPERATURE

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ABSTRACT

Mixed CH₄-THF hydrate formation has been investigated at ambient temperature (298 K) with focus on advancing the commercial feasibility of solidified natural gas (SNG) technology for natural gas storage. In addition to freshwater, direct use of seawater has also been studied for hydrate formation. There is quite a gulf between the two systems at the chosen experimental temperature of 298 K with final gas uptake for the freshwater system being more than double that of its seawater counterpart while the kinetics of hydrate formation also shows a marked difference, in favor of freshwater. To improve the kinetics of hydrate formation from seawater, possible use of two kinetic promoters, hydrophilic amino acid L-Arginine and hydrophobic amino acid L-Tryptophan has been proposed. Both kinetic promoters used enhance the kinetics of hydrate formation from seawater and while the final gas uptake is roughly equivalent for the systems without any promoter and with hydrophobic L-Tryptophan, presence of hydrophilic amino acid L-Arginine increases the final gas uptake obtained for seawater as well.

Keywords: Solidified Natural Gas, Gas Hydrate, Gas Storage, Kinetics, Amino Acids

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NONMENCLATURE

Abbreviations

| | | | |
|-----|------------------------|-----|------------------------|
| THF | Tetrahydrofuran | SNG | Solidified natural gas |
| STR | Stirred tank reactor | SI | Structure I hydrate |
| UTR | Unstirred tank reactor | SII | Structure II hydrate |

1. INTRODUCTION

Safe and economical storage of natural gas has always been a point of contention for all concerned with conventional methods such as liquefaction and compression posing teething challenges. While storage in the form of liquefied natural gas (LNG) requires going down to extremely low temperatures (−162 °C at 0.1 MPa), following the compressed natural gas (CNG) route involves storing natural gas under extremely high pressures (~20.0-25.0 MPa at ambient temperatures) [1, 2]. The extreme temperature and pressure conditions required to store natural gas in the form of LNG or CNG and the high associated risk and financial input of the same have led researchers to look for alternative options that might be able to offer natural gas storage with much safer and economical returns. To this effect, solidified natural gas (SNG) technology, which basically involves trapping the gas in the form of solid clathrate hydrates has proven to be the one to watch out for, with its high volumetric capacity or compact mode of storage and non-explosive character [2-4]. By transitioning from SI to SII hydrates using the addition of thermodynamic promoters like Tetrahydrofuran (THF) to the system, researchers have also been able to significantly reduce the overall operational cost of the process by bringing down the hydrate equilibrium conditions and thus both, hydrate formation and subsequent storage conditions to more favorable ones. Attempts at further economizing the process have also been made by directly using seawater instead of freshwater to form mixed CH₄-THF hydrates [2, 5].

The current study aims to advance the technical and commercial feasibility of SNG technology by studying mixed CH₄-THF hydrate formation at ambient temperature (298 K). Freshwater and seawater were used individually for hydrate formation and the kinetics obtained compared. The effects of benign kinetic

promoters (hydrophilic and hydrophobic amino acids) on hydrate formation kinetics were also investigated.

2. EXPERIMENTAL SECTION

Methane gas (99.9% purity) purchased from Air Liquide Singapore Pte Ltd. was used for all experiments. Hydrophilic amino acid L-Arginine (reagent grade, $\geq 98\%$ purity) and hydrophobic amino acid L-Tryptophan (reagent grade, $\geq 98\%$ purity) used were purchased from Sigma-Aldrich. Tetrahydrofuran (THF) - 99.99% purity was purchased from Fisher Chemicals. Ultrapure water (Merck Millipore) was used for all experiments.

Details of the experimental setup (including schematic) used for the current study can be found elsewhere in literature [6]. Pressure and temperature conditions used for hydrate formation were constant throughout the study at 9.5 MPa and 298 K respectively. The method used for hydrate formation was what is known as a combinatorial hybrid approach and involves the use of both fundamental stirred tank reactor (STR) and unstirred tank reactor (UTR) configurations generally used for hydrate formation. For all the experiments performed in the present study, after CH₄ gas (up to the desired experimental pressure) had been injected into the system, the system was left undisturbed for fifteen minutes to allow for the gas to dissolve into the aqueous phase and attain equilibrium. At the fifteen minute mark from the end of gas injection, stirring (400 rpm) was initiated in the system with the help of a magnetic stirrer. Stirring was allowed to proceed until the onset of hydrate nucleation and for a maximum of three minutes. In essence, all of the systems studied nucleated within the three minute stirring period. The onset of nucleation was determined using simultaneous visual observation of hydrate crystals through viewing windows present in the reactor setup and characteristic exothermic nucleation peak in the temperature profile inside the reactor. The hybrid process greatly reduces nucleation stochasticity while enhancing hydrate growth kinetics and is especially beneficial for the current study as the selected aforementioned hydrate formation conditions offer extremely low driving force for hydrate formation; (~ 5.4 MPa for freshwater and ~ 2.4 MPa for seawater) [7].

The procedure used for calculating the gas uptake due to hydrate formation is the same as that used for one of our previous studies and can be found in literature [6].

3. RESULTS AND DISCUSSION

Figure 1 shows a sample morphology observation for hydrate formation as made in the current study. This

figure has been provided mainly to give an understanding to the readers of how morphology observation can allow the determination of the nucleation point for hydrate formation. Within Figure 1, sub figure (i) represents the point where hydrates nucleated. From Figure 1(i), small hydrate crystals can be observed on the wall of the window and on the gas-liquid interface. This figure has been blown up and is shown as sub figure (b) in Figure 1 where it has been compared to the solution and the gas liquid interface as they appear just prior to hydrate nucleation (sub figure (a)). As is evident, there is a marked difference in the appearance of the hydrate forming solution and gas-liquid interface just prior and subsequent to hydrate nucleation. While the solution appears clear before hydrate nucleation, it becomes murky as soon as the nucleation event occurs indicating the presence of hydrate crystals within the liquid phase. The gas liquid interface meanwhile turns from clear to being dotted with short pointy hydrate crystals. An example of how the morphology of hydrate formation proceeds (2 hours of growth from the nucleation point in this case) can be noted by following sub figures (ii) to (x) in Figure 1.

Figure 2 compares the gas uptake due to hydrate formation when the water used to form hydrates was a) freshwater and b) seawater. Gas uptake shown in Figure 2 is only for the first five hours of hydrate growth i.e. the first five hours after hydrate nucleation. For this study, that would represent a period of five hours once stirring had been stopped. Of additional consideration is that only one set of experimental data has been shown for each system represented in Figure 2. As seen from the figure, there is a large divide in the performance, i.e. hydrate formation kinetics and final gas uptake, when individually using freshwater and seawater to form hydrates for methane storage. While the gas uptake obtained with freshwater after five hours of hydrate formation was pretty high (just above 55 mmol of gas consumed per mol of water), the same was cut to less than half (just above 24 mmol of gas consumed per mol of water) for seawater. The kinetics of hydrate formation too took a severe hit on moving from freshwater to seawater with the gas uptake at the end of one hour of hydrate formation going down from little above 40 mmol of gas per mol of water to just about 16 mmol of gas per mol of water. This dip in performance is expected though, as salts such as NaCl present in seawater are expected to act as thermodynamic inhibitors making it quite difficult for hydrate growth to initiate and sustain [7, 8]. Though the thermodynamic promoter THF fights

this action of the salts to a certain extent by allowing hydrate to nucleate and grow in the first place, it is unable to replicate the sort of rapid kinetics and high gas uptake for hydrate formation that is achieved with freshwater. The functionality of the thermodynamic promoter is also severely limited by the fact that the driving force offered to the seawater system at the current experimental conditions is rather low.

It can be seen from Figure 3 that both kinetic promoters used do indeed show a certain level of enhancement in the kinetics of hydrate formation as compared to the system without any promoter but there is not much difference in the final gas uptake obtained after five hours for all three seawater systems. In presence of the kinetic promoters, the rate of gas uptake sees a significant improvement in particular, during the

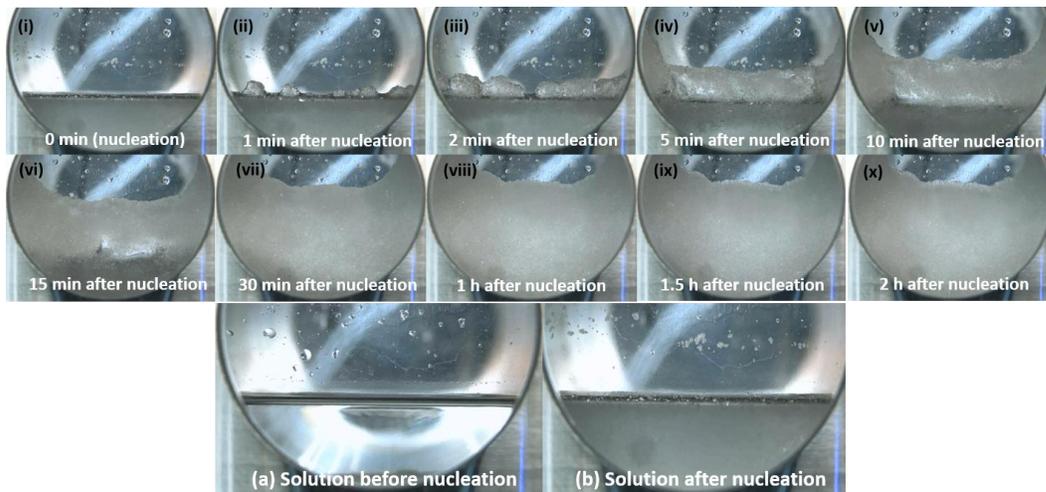


Fig 1: Typical morphology observation for hydrate formation indicating hydrate nucleation and mapping hydrate growth

In order to combat the roadblocks presented by the salts inherently present in the seawater system, it was proposed to use some benign kinetic hydrate promoters in low concentrations and try to speed up the hydrate formation process. Two different amino acids, hydrophilic L-Arginine and hydrophobic L-Tryptophan were chosen for this purpose. The hydrophilic or hydrophobic nature of a kinetic promoter can have a large say on its activity and this has been well documented in literature [9-12]. The effectiveness of kinetic promoters can also be extremely system dependent and thus it was decided to use one kinetic promoter of each kind (hydrophilic and hydrophobic) to evaluate their respective effects on mixed CH_4 -THF hydrate formation at the current experimental conditions. Both L-Arginine and L-Tryptophan were used at the relatively low concentration of 300 ppm for the present study. Figure 3 compares the gas uptake obtained due to hydrate formation for the different seawater systems studied. Again, gas uptake shown is only for the first five hours of hydrate growth (as explained earlier) and for a single set of experiments for each system represented. Readers might note that the “seawater+THF” data shown in Figure 3 is the same as was shown in Figure 2.

first couple of hours of hydrate formation and this holds true for both kinetic promoters studied. This is a good result from the point of view of SNG technology as any commercial process would expectedly only have a short hydrate formation stage with rapid kinetics where maximum water to hydrate conversion and gas uptake would be achieved within the shortest possible time. For a long hydrate formation process, the final gas uptake obtained for various systems is generally expected to be quite close. The same is observed in Figure 3 as far as the “seawater+THF+L-Tryptophan” and “seawater+THF” systems are concerned with the final gas uptake (at the end of five hours) beginning to even out for these two systems. However, the final gas uptake is slightly enhanced when using L-Arginine, the hydrophilic amino acid as the kinetic promoter. The enhancement though is not significant enough to make too pronounced a difference on the big scheme of things and hence not much is made of it at this point of time. It cannot definitely be said as to why the hydrophilic amino acid shows a slightly better performance than the hydrophobic amino acid as the activity of amino acids is greatly system dependent. In general, owing to their structural similarities, amino acids are generally thought to act the same way as surfactants when it comes to their use as kinetic promoters, albeit without the huge

amount of foam formation generally observed with surfactants [9-11, 13] It has previously been reported that hydrophilic amino acids can act as kinetic promoters especially when CH_4 is present as the hydrate forming gas [10]. In fact L-Arginine itself has been reported to show significant kinetic enhancement for pure CH_4 hydrate formation, so the result obtained in the present study is not all that unexpected [9, 13].

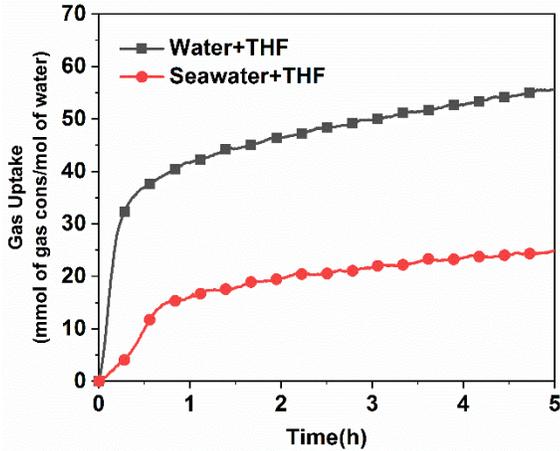


Fig 2: Comparison of the gas uptake for hydrate formation using freshwater and seawater and no kinetic promoter

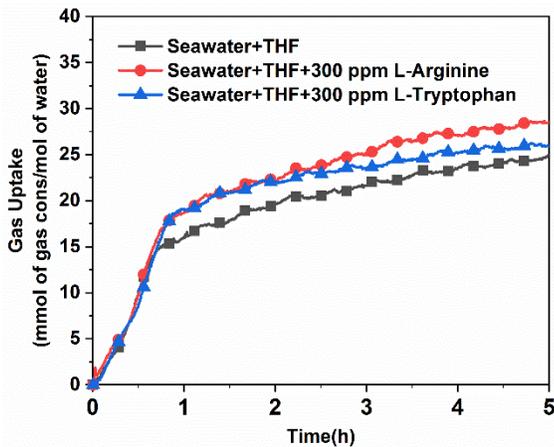


Fig 3: Comparison of the gas uptake for the different kinetic promoters studied; seawater used for hydrate formation

Although both hydrophilic and hydrophobic kinetic promoters had a positive impact on mixed CH_4 -THF hydrate formation using seawater, the enhancements in hydrate formation kinetics and gas uptake obtained weren't significant enough to push the performance of seawater close to that observed when hydrate formation was carried out using freshwater. The positives gained from the use of the kinetic promoters in the present study should be applied in a manner so as to build on them in future studies. It is quite clear that the use of kinetic promoters does indeed have a substantial effect

on the hydrate formation process, especially the initial kinetics. Varying the concentration of these additives might be able to unlock their true potential and this is something that should definitely be investigated in future studies. Moreover, the impact of these kinetic promoters on the kinetics of hydrate formation using freshwater is also of great interest. From a commercial viewpoint, if the kinetics for the freshwater system at ambient temperature can be further boosted, it would put the SNG technology using thermodynamic promoter THF in great stead. Commercial interest can be even further enhanced if the pressure required for hydrate formation can be decreased using the hybrid combinatorial approach and suitable kinetic promoters. In the present study, the pressure used for hydrate formation was 9.5 MPa for freshwater and seawater alike. Utilizing the hybrid combinatorial approach and the correct kinetic promoters might allow the option of bringing down the initial experimental pressure, at least as far as the freshwater system is concerned and this should be one of the key points of focus for the following mixed CH_4 -THF hydrate formation studies at ambient temperature.

It should be noted that although the data presented in Figures 2 and 3 was only for a single experimental run for each system studied, this data is in fact repeatable. The repeat runs for the various systems however, have not been plotted in Figures 2 and 3 for the sake of brevity.

4. CONCLUSIONS

The present work considered mixed CH_4 -THF hydrate formation at ambient temperature (298 K) with the objective of enhancing the commercial feasibility of SNG technology. Comparison of hydrate formation at 298 K using freshwater and seawater individually, revealed that the kinetics and final gas uptake were significantly higher in the case of freshwater owing to the higher driving force available. To counter the inhibiting effects of salts inherently present in seawater, two benign amino acids (hydrophilic L-Arginine and hydrophobic L-Tryptophan) were proposed to be used in low concentration (300 ppm) as kinetic promoters. Results obtained show that both kinetic promoters used enhance the kinetics of hydrate formation as compared to the system containing only seawater and THF. While over time, the final gas uptake for the "seawater+THF" system and "seawater+THF+L-Tryptophan" system begin to even out, presence of the hydrophilic promoter

L-Arginine shows a slight enhancement in the final gas uptake too. The enhancements obtained in hydrate formation kinetics and gas uptake in presence of the kinetic promoters however, is still not enough to push seawater as an attractive alternative to freshwater for hydrate formation, at least as far as formation at temperature (298 K) is concerned. The results obtained and conclusions drawn from this study should serve as a fundamental benchmark and guide subsequent associated research as we further our knowledge of mixed CH₄-THF hydrate formation and look to constantly augment the commercial feasibility of SNG technology.

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