Investigation on the effect of THF on Nitrogen Hydrate formation under isobaric condition

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Abstract. In this paper, we studied nitrogen (N₂) hydrate formation in the presence of tetrahydrofuran (THF) under 3 different conditions; different concentration of THF (0, 3 and 30 % (v/v)), different temperature setting (room temperature and induced temperature) and different water content (15, 35 and 55 mL) in an isobaric condition. We found that in the presence of THF which acting as an enhancer, hydrate formation kinetic is highly influenced by these parameters. We observed a striking contrast in hydrate formation behaviour observed at room temperature (RT) and induced temperature (IT) with and without the presence of THF under similar operating conditions. At the presence of 30 % (v/v) of THF in 15 mL water, it can be seen that, hydrate tend to form faster than other samples. Visual observation of N₂ hydrates are also conducted at 30 % (v/v) of THF in 15 mL water.

1. Introduction
Gas hydrate is a crystalline solid that compose mostly of compacted water and gas molecules, which formed at low temperature and high pressure conditions [1]. The formation of hydrate comprises of certain light gases such as methane, ethane, propane, carbon dioxide and nitrogen. The size and shape of hydrate formed depend on the atomic size of gas used and the formation condition that is applied. The most commonly encountered structures are the cubic structures I (sI) and II (sII) [2]. Gas hydrate formation was one of the flow assurance main problems in oil and gas industries [3]. Thus, the gas hydrate particles can agglomerate and progressively build up into a large lump which had the potential to block the flowlines, chokes, valves and also other equipment along the pipelines [3-4]. Hydrate is useful in many industrial applications like storage and transport of natural gas, gas separation, seawater desalination, CO₂ capture, CO₂ sequestration and seawater desalination [5-9]. In recent time, storage of gas in the form of hydrate gains interests due to high gas contents per volume of hydrate, environmentally friendly and as well as its non-explosive nature that possesses no safety risk. Despite

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all the applications of hydrate, the hydrate phase equilibria of the carbon dioxide, nitrogen, and water are scarcely studied. Especially in nitrogen hydrates, most of the researchers focus on their application for the dissociation of hydrates in sediment [10]. Nitrogen hydrates were among the hydrate that requires an extreme amount of pressure (up to 1000 atm) to form. Reducing hydrate formation pressure is a hindrance issue for the wide application of hydrate technology.

Tetrahydrofuran (THF) is known as one of a thermodynamic promoter that functions to reduce hydrate formation pressure for methane, ethane, carbon dioxide and nitrogen [11]. It had been proven that THF can form stable sII hydrates with water at atmospheric pressure when the temperature is below 278 K [12]. Therefore, THF is added as guest molecules for the formation of nitrogen hydrates to help stabilize the hydrate cages thereby reducing the formation pressures of nitrogen hydrates. THF is frequently used as a model system for the study of hydrate formation because of the elimination of the mass transfer effect [13]. The use of THF as thermodynamic promoters had been used in previous research, where they use multiple mixed systems, among these, are THF+hydrogen+water [14], [15], THF+carbon dioxide+water [16], THF+methane+water [16], [17], THF+methyl fluoride+water [18] and THF+carbon dioxide+nitrogen+water [19]. Recently, Veluswamy et al. [20] was able to form the hydrate in the laboratory scale in an isobaric system in the present of THF as promoter but at a very high pressures of 30 bar and 283.2 K using methane gas. In this study, the objective was to achieve the enhancement in hydrate formation kinetics for N\textsubscript{2} hydrates in the presence of THF in an isobaric condition at lower pressure and temperatures. The effect of promoter, temperature and volume upon the hydrate formation was also investigated.

2. Experimental Section

2.1 Preparation of Material

High Purity Nitrogen (99.9\%) supplied by Pure Dimension Enterprise were used in the formation of hydrates. The promoter used was the analytical reagent grade tetrahydrofuran (THF), supplied by the Fisher Chemical Sdn. Bhd. In this work, the solution used is the mixture of distilled water + THF. All of the solutions were prepared at the room temperature and atmospheric pressure. The preparation of THF solution was done by the following steps: A certain amount of water and THF were weighted successively. Next the water was poured into THF as quickly as one can to avoid volatilization of THF, and subsequently the solution was introduced into the pressure cell after being stirred with a glass rod. Water and THF were weighed on an electronic balance with an accuracy of (0.1 mg).

2.2 Experimental Apparatus

A schematic diagram of the experimental apparatus used to determine the hydrate formation is shown in figure 1. The main part of the apparatus is the high pressure cell with an effective volume of 110 cm\textsuperscript{3}. The pressure of the cell is controlled by rotating the control knob on to the desired pressure. The pressure cell was secured inside a customized box which acts as the cooling jacket to maintain the experimental temperature inside the pressure cell. The pressure and temperature measurement were made by reading on the pressure that was shown on the pressure gauge attached to the cell as well as from the P-T controller. All of the processes require collection of data manually (table A.1 and table A.2) as the reactor does not connect to any data acquisition (DAQ) system. All experiments performed in a quiescent (unstirred) pressure cell.
2.3 Experimental Method
Schematic of the experimental procedure is shown in Figure 1. Aqueous solutions (55 cm$^3$) comprise of different concentration of THF (0% (v/v), 3% (v/v) and 30% (v/v) of THF solution) were prepared and introduced into the cell. The cell and tubing were purged thrice using the nitrogen gas to remove the air remaining and the pressure cell is vacuumed to experimental pressure. The temperature was set at room temperature. The experiment is done in an isobaric system, where the pressure was kept constant throughout the experiment. Once the experimental pressure in the vessel reached desired values, the outlet valves of the cell then closed to concentrate the gas inside the cell. The aqueous solution inside the pressure cell remained quiescent. Temperature was recorded every 1 hour for six (6) hours. Hydrate formation was detected by a sudden increase in temperature. The time before temperature reading remains stabled is recorded as hydrate induction time.

3. Result and Discussion

3.1 Effect of temperatures and different concentration of THF on hydrate formation.

The pressure required for the formation of hydrate using (N$_2$) gas is high for a commercial industrial process [21]. This implies significant compression would be required. Therefore, the use of THF has been proposed by Linga et al. [22]. The used of THF is an efficient method for stabilizing the nitrogen hydrates [23]. Usually, the hydrates will form at a pressure of 50-100 bar, but with THF it can be reduced until 5-10 bar at the temperature range between 0 - 10°C [24]. All the experimental results are summarised in table A.1 and table A.2. Figure 2 and figure 3 shows the graph of the effect of different temperatures, one is at room temperature (RT) and at induced temperature (IT) on different concentration of THF. As seen from the graph, there is a huge difference between the 0% (v/v), 3% (v/v) and 30% (v/v) RT and IT. During the hydrate formation at room temperature (RT), there is no trace of nitrogen hydrate formed in any of the THF concentration. There is no significant peak is seen and the graph is aligned almost similar to a straight line. The absence of significant peak deduces that there is no hydrate is formed as hydrate formation is an exothermic process [25]. This may also can be linked to less N$_2$ gas is trapped at high temperature during the nucleation process [26]. Ross et al. [27], in their studies also mentioned that thermal conductivity of THF in hydrate is proportional to temperature and not pressure. There is also a possibility that with the addition of THF in water allow the shift of the promotion effect of THF to inhibition effect at a certain concentration. In all three (3) THF concentrations, none of them performed at room temperature. However, the nucleation process still occurred as the end product (aqueous solution), is in a fizzy and cloudy state. Devarakonda et al. [28] mentioned that the point when the solution turns cloudy is considered the end of nucleation. Perhaps in
the next experiment, the time to form N₂ gas hydrates could be lengthened to see whether hydrate will be formed at room temperature. It has been stated in the previous study, in the study of hydrate formation by using THF in order to shorten the induction time the only suitable medium is in an induced system [29]. Nonetheless, hydrate may form if the right temperature and pressure condition are designed.

Figure 2. Hydrate formation for the nitrogen+water+THF system at room temperature: 30 %(v/v) THF, 3 %(v/v) THF and 0 %(v/v) THF.

Figure 3: Hydrate formation for an induced temperature nitrogen+water+THF system: 30 %(v/v) THF, 3 %(v/v) THF and 0 %(v/v) THF.

Figure 3 shows the result of hydrate formation at three (3) different concentration of THF (0 %(v/v), 3 %(v/v) and 30 %(v/v)). From the figure, it can be seen that for all 3 concentration in the same induced system, the trend in temperature decrease is different for each concentration. The higher the concentration of THF, the lower the hydrate stability temperature. The temperature continuously decreases until the 2nd hours, at 282.25 K, 281.55 K and 275.75 K for 0 %(v/v), 3 %(v/v) and 30 %(v/v). It can be assumed that the high cooling rates create supercooled water at a temperature of 273.15 K – 278.15 K. Reducing temperature may increase the probability of thermodynamically stable nucleation [30] until the temperature reaches a point that the nucleation is not a random process anymore and stable nuclei (hydrate) become available and grow spontaneously. Similar trend were found by Kang et al. [19], which uses an isochoric method, they observe a remarkable decrease of dissociation pressure for the entire temperature range. It could be the point before 2nd hours is called the induction time.
After the 2nd hours, it can be seen from figure 3, for 0 %/(v/v) from 3rd to 5th hours, there is no significant increment in temperature. While for 3 %/(v/v), from 3rd to 5th, the increment in temperature started at the 5th hours. Only at 30 %/(v/v) THF concentration the temperature keep rising from the 3rd to 5th hours of running. At this stage, it could be the growth of supercritical nuclei which usually controlled by mass and heat transfer [31]. It is obvious that at 30% concentration of THF is the fastest time (3rd hours) stable hydrate was formed compared to the other concentrations (0 %/(v/v) at 6th hour, 3 %/(v/v) at 5th hour). The increasing of THF concentration from 0 %/(v/v) – 30 %/(v/v) used in our work caused a substantial decrease in the observed induction time.

3.2 Effect of volumes of aqueous solution.

In this section, the highest THF concentration at 30 %/(v/v) is used, as in section 3.1, at 30% of THF, hydrate induction time are reduced. From figure 4 and figure 5, it can be seen that at 15 mL, hydrates formed earlier compared to the 35 and 55 mL of (water+THF) at the first 4th hours. All the bonds in hydrates are hydrogen bonds. Water’s readiness to make these bonds is responsible for the stability of gas hydrates [32]. It is discovered that when a volume of water to nitrogen ratio are diminished, hydrates can form faster. Hence, the lower the volume, there will be more space available for water molecules to form cages, connected by hydrogen bonding and for N2 gas molecules to fill in these cavities. The concentration of THF also helps to reduce the equilibrium formation conditions enabling hydrate to form at much lower pressures. THF was found to reduce the induction time and increase the rate of hydrate growth [33]. The effect of volume with the addition of THF as promoter, gives significant effect on the rate of hydrate formation. It is also shown that, if a lower volume of water is used, it will influence the rate of hydrate formation. Moreover, for high volume of water, the time needed for hydrate to form is longer. From a comparison of the variation amounts of volume, the gas consumption due to the hydrate formation at high volume is significantly higher than that at low volume. As the gas solubility at high volume is even lower than at low volume and the decrease of the system temperature is largely derived from the formation of hydrate [34].

4. Conclusion
The effect of THF on N2 hydrate formation under isobaric condition was studied in three (3) different parameters at different temperature setting, different THF concentration (0 %/(v/v), 3 %/(v/v) and 30
% (v/v)) and on different volume of water +THF mixtures. There was no hydrate formed at room temperature in all three (3) THF concentrations. However, hydrate may form if the running time is lengthened. This is something that could be done in the future research. In an induce temperature, the induction time is lowered in increasing THF concentration from 0 % (v/v) – 30% (v/v). 30 % (v/v) was used to study the effect of volume (15, 35 and 55 mL) on N₂ hydrate formation and it can be seen that at 15 mL, hydrate tend to form faster. This is because more space is available for water molecules to form cages and for small N₂ gas molecules with the help of THF as promoter to fill in these cavities and form sII hydrate structure. This study in general provides motivation and useful information to develop more effective way to form N₂ hydrate at low pressure and various temperatures setting in the laboratory scale, which may help in natural gas storage application for domestic and industrial purposes.

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Appendices

Table A.1. Room temperature system with different THF concentration.

| Time (hr) | 0 % (v/v) | 3 % (v/v) | 30 % (v/v) |
|-----------|-----------|-----------|------------|
|           | THF       | THF       | THF        |
| 0         | 25        | 24.8      | 24         |
| 1         | 24.5      | 23.4      | 23.3       |
| 2         | 24.1      | 23.2      | 23.2       |
| 3         | 23.9      | 23.1      | 23.3       |
| 4         | 23.8      | 23.5      | 23.4       |
| 5         | 23.8      | 23.6      | 23.5       |
| 6         | 23.9      | 23.7      | 23.7       |

Table A.2. Induced temperature system with different THF concentration.

| Time (hr) | 0 % (v/v) | 3 % (v/v) | 30 % (v/v) |
|-----------|-----------|-----------|------------|
|           | THF       | THF       | THF        |
| 0         | 25        | 24.3      | 20.1       |
| 1         | 15.3      | 12.2      | 3.8        |
| 2         | 9.1       | 8.4       | 2.6        |
| 3         | 8.6       | 7.6       | 2.9        |
| 4         | 7.5       | 7.8       | 4.7        |
| 5         | 7.8       | 8.9       | 6.8        |
| 6         | 8.2       | 10.5      | 8.4        |
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