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## Effect of POM on Formation Kinetics of Methane Hydrate

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**Abstract:** The kinetics of formation of methane hydrate in deionised water in presence of Potassium Oxalate Monohydrate (POM) is studied in a batch reactor which is designed and built for a laboratory scale used. In this experimental study, the formation of methane hydrate in deionised water (18Ω) is investigated at fixed temperature of 273.15 K and pressures of 65, 60, 55, 50, 40 bar, respectively. The formation of methane hydrates in POM solutions are investigated by using various concentrations of POM up to 2000 ppm at temperature of 273.15 K and 65 bar pressure. For methane hydrate, the induction time decreases with the increase of initial pressure due to the increase of sub cooling and driving force in the system. Moreover, experimental results show that the addition of POM reduces the induction time required for hydrate formation and significantly increases the carbon dioxide and methane uptake and these effects are concentration dependant. Furthermore, the addition of POM in the hydrate forming systems has been shown to improve the apparent rate constant of the system.

**Key words:** Kinetic, clathrate hydrate, methane hydrate, POM

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### INTRODUCTION

Clathrate hydrates or gas hydrates are ice like inclusion compounds which is formed by physically-stable interactions between water and guest molecule entrapped in the cavities built by water molecules under low temperature and high pressure conditions (Sloan and Koh, 2008). These cavities have to be at least partially filled with the guest molecules in order to stabilize the structure. The type of cavities that are formed and the distribution of those cavities in a unit cell are used to distinguish clathrate hydrate structures. There are three common types of hydrate structures which are I, II and H (Sloan and Koh, 2008). Low molecular weight gases such as methane and carbon dioxide, form structure I in hydrate equilibria. Structure I hydrate able to occupy by at most eight guest molecules like methane, ethane, carbon dioxide and hydrogen sulfide (Sloan and Koh, 2008; Carroll, 2003).

In the recent day, the rise of interest in gas hydrates technology was due to its potential as a new potential source of natural gases (Klauda and Sandler, 2005), a potential unit operation for seawater desalination, gas fractionation, gas storage (Makogon *et al.*, 2007) and other novel applications like carbon dioxide capture, storage and sequestration (Tajima *et al.*, 2004;

Englezos and Lee, 2005; Linga *et al.*, 2007). This novel application of capturing carbon dioxide (CO<sub>2</sub>) is been proposed for its potential for CO<sub>2</sub> sequestration and methane recovery from natural gas hydrates in and CO<sub>2</sub> capture from flue gases to reduce atmospheric emissions (Belandria *et al.*, 2010; Eslamimanesh *et al.*, 2012; Kumar *et al.*, 2013). This method promises to be less energy intensive and able of treating multi component gases stream with high concentration CO<sub>2</sub> (Duc *et al.*, 2007; Sabil *et al.*, 2010a). However a commercially viable hydrate based technology demands a rapid hydrate formation rate.

The hydrate formation rate can be affected by many factors such as the level of supercooling, the speed of agitation, the presence of additives and others (Sloan and Koh, 2008). Hence, several methods have been proposed to enhance the hydrate formation, including chemical and mechanical methods. The chemical method used to enhance hydrate formation is by adding certain amount of thermodynamics hydrate promoters such as tetrahydrofuran and tetrahydropyran (Mooijer-van den Heuvel *et al.*, 2001; Sabil *et al.*, 2010b). It has been shown in several studies that the inclusion of these promoters can promote hydrate nucleation and accelerate hydrate growth. Based on the previous studies, it is shown that the addition of these

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promoters can reduce induction time, reduce the super cooling degree for crystallization and increase the amount of water converted into hydrate (Mori, 2003; Sabil *et al.*, 2010a). The inclusion of these hydrate promoters will reduce the pressure requirement or increase the temperature at which the clathrate hydrates are stable. Hence, the energy required for pressurization or cooling of the systems will be reduced. However, the concentration of these hydrate promoters required for effective promoting effect are relatively high at about 7 mol%. Since these promoters are also trapped in hydrate cavities, the amount of cavities in hydrate lattice that are available for capturing gas molecules is also reduced (Eslamimanesh *et al.*, 2012). Therefore, the usage of these promoters is less practical due to these limitations. New type of hydrate promoters that can be used at lower concentration and do not affect the amount of cavities in hydrate lattice is required for the improvement of hydrate based separation system.

Zhong and Rogers (2000) introduced the new type of promoters which is named as kinetic hydrate promoter. They claimed that the micelles formation will increase the solubility of the gas into aqueous phase and enhance the hydrate formation rate by inducing the formation of hydrate crystals around the micelle in the bulk water phase (Gayet *et al.*, 2005). Recently, a study found that micelles formation could not be the correct mechanism for promoting the hydrate formation of Sodium Dodecyl Sulfate (SDS) solution. While the promotion mechanism of SDS in hydrate formation process still is not clear, visual observation showed that in the presence of SDS, hydrate crystals tend to move forward to the reactor's wall (Gayet *et al.*, 2005). This SDS prevents hydrates particles from agglomerating in which they absorbs the liquid from the bulk to the crystallization front where the gas-liquid interface is renewed and hydrates grow at a higher rate without any mechanical agitation. Besides that, there have been few studies been conducted on the inclusion of Potassium Oxalate Monohydrate (POM) as kinetic hydrate promoter but its effect on hydrate formation rate is not very clear. Zhang *et al.* (2004) reported that POM is able to increase the formation rate of natural gas hydrate in where the natural gas hydrate formed rapidly which is several times faster than without additives. Then, Li *et al.* (2005) claimed that the addition of potassium oxalate monohydrate in water has shown no effect on the nucleation and growth of HCFC141b gas hydrate. The POM is known as a salt solution and with low concentrations, it may promote hydrate formation. Therefore, SDS and POM seems to be a good candidate to be used as low dosage hydrate promoters.

In this study, the kinetics of formation of methane hydrate in presence of POM is studied. The main focus of this study is to study the effects of POM on the kinetic formation of methane hydrates. In this study, an apparatus for the measurement of the pressure-temperature data during hydrate formation was designed and built. The induction time and the apparent rate constant for methane hydrates in deionised water in presence of POM solutions are reported and discussed.

## MATERIALS AND METHODS

**Materials:** Methane was supplied by the MOX-Linde Gases Sdn. Bhd. with a minimum purity of 99.95%. Deionised water was supplied by Chemical Eng. Department of Universiti Teknologi PETRONAS. Potassium oxalate monohydrate was purchased from Merck with purity of 99.5% (POM).

**Apparatus:** Figure 1 shows the schematic representation of the high-pressure system used for kinetics consists of a high-pressure stainless steel vessel with an measurement. The apparatus was built based on the design reported by Sabil *et al.* (2009). The apparatus internal volume of 500 mL. The maximum working pressure for the vessel is 300 MPa. The vessel is immersed in a

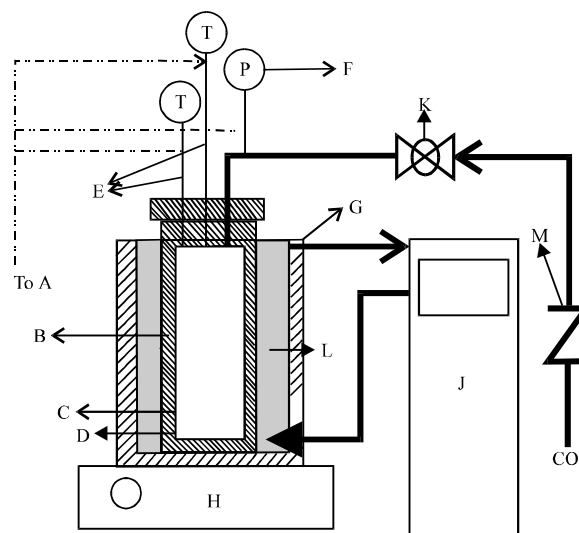


Fig. 1: Schematic representation of the high pressure kinetics measurement apparatus: A: Data acquisition system, B: High pressure vessel, C: Liquid sample, D: Stirrer, E: Thermocouple, F: Pressure gauge, G: Water bath, H: RPM controller, J: Cryostat, K: Valve, L: Thermostatic liquid, M: One-way valve

water bath to keep the temperature constant at a desired value. The temperature inside the vessel is monitored both in the gas phase and in the liquid phase by two thermocouples with an accuracy of  $\pm 0.01^\circ\text{C}$ . The temperature of the thermostatic bath is controlled by a PID controller that maintained at a desired temperature within  $\pm 0.1^\circ\text{C}$ . Proper mixing in the liquid sample is achieved through magnetic stirrer which is placed in the vessel. The pressure inside the cell is measured with a pressure transducer. The pressure and temperatures data was recorded and stored in a data acquisition system.

**Kinetic measurement procedure:** In this study, two different liquids are used which are deionised water aqueous solution and mixture of deionised water potassium oxalate monohydrate solution. During the experiment, no further addition of methane or liquid samples is made as all of these components need to be kept constant. The cell is loaded with 100 mL of liquid sample for each run and the liquid sample is prepared for two different liquid with various concentration. Before the experiment is started, the excess air inside of the cell need to be removed by flushing the cell with the carbon dioxide or methane gas for five to six times. This step need to be repeated for five or six time in order to ensure the repeatability of the experimental results as the presence of other gases may affects the formation conditions of hydrate. After the flushing procedure is completed, the cell is ready to be used for the measurement of kinetics.

The loading of carbon dioxide or methane gas are made at a specified pressure with the initial temperature is being set to 2-3 K higher than the hydrate equilibrium temperature due to the solubility of that gases. Then, when the temperature becomes steady, the cell is pressurized with carbon dioxide or methane gas to the desired pressure value. Next, the stirrer is switched on. After a while, the temperature is set back to the desired experimental temperature which is 275.15 K and this step is done when only the pressure is already stabilized. The final temperature for all experiments in this study is set at 275.15 K. Then, when the desired experimental temperature is achieved, the system is left until the pressure and temperature value of the system become stable. Finally, when the pressure and temperature value of the system remain unchanged for 2-3 h, this indicates that the gas hydrate formation is completed and the experiment can be ended.

**RESULTS AND DISCUSSIONS**

In this study, two sets of experiments were carried out for methane hydrate which are: (1) Methane+deionised

water at different initial pressures; (2) Methane+POM solution at various concentration of POM up to 2000 ppm with the operating condition of 65 bar and 273.15 K. The effect of initial methane p pressure to the induction time for methane hydrate formation is plotted in the Fig. 2. As presented in this figure, the induction time for methane hydrate in deionised water decreases as the initial methane pressure increases. Induction time is obtained by observing the pressure time relationship. As depicted in this figure, the induction time decreases from 6.71-3.94 h as the initial methane pressure increases from 40-65 bars. This behavior is may be attributed by an increase in methane initial pressure causes a richer environment of super saturation at the liquid/vapour interface which is essential for the formation and growth of hydrate nucleus . In addition, higher degree of sub-cooling is achieved in the system as the initial methane pressure increases as shown in Fig. 3. The degree of sub-cooling is defined as the difference between the hydrate equilibrium temperature and the temperature at the turbidity point (Watanabe *et al.*, 2005; Arjmandi *et al.*, 2005). Arjmandi *et al.* (2005) have shown

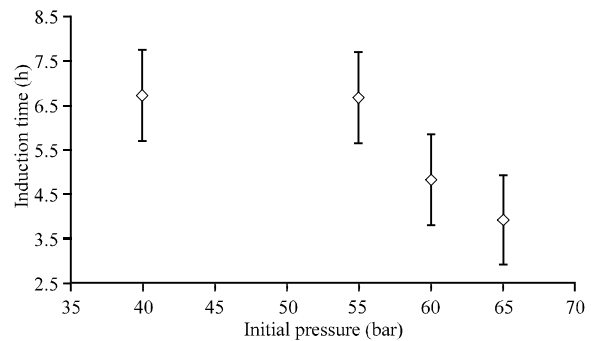


Fig. 2: Induction time of methane hydrate in deionised water at different methane initial pressures

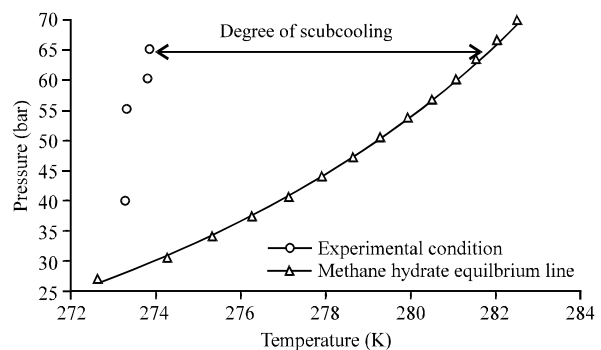


Fig. 3: Degree of subcooling between the experimental conditions and methane hydrate equilibrium

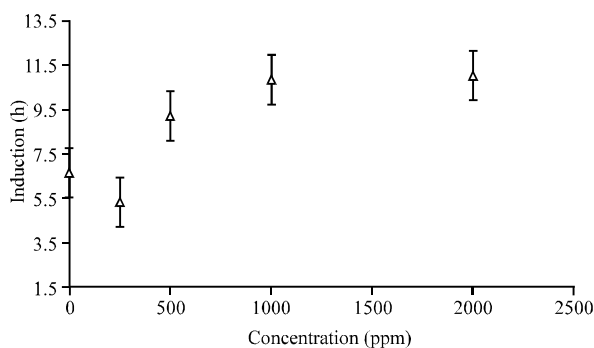


Fig. 4: Induction time of methane hydrate in various concentration of POM solution

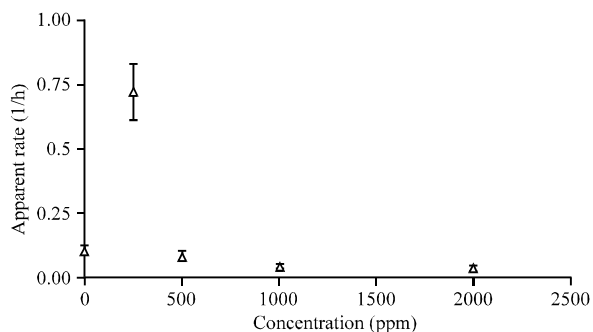


Fig. 6: Apparent rate constant of methane hydrate at various concentrations of POM

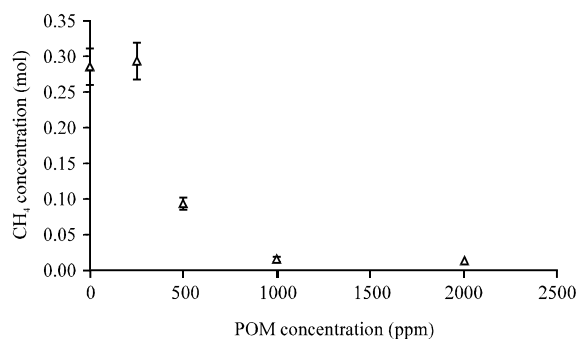


Fig. 5: Methane consumed during hydrate growth for methane hydrate in various concentration of POM solution

that sub-cooling is the proper representation of hydrate formation driving force for the simple hydrates such as carbon dioxide and methane hydrate as driving force is directly proportional to the degree of sub-cooling. Then, with the increased of driving force, the system is expected to be more susceptible for formation of hydrate and this behaviour causes the reduction in induction time as shown in this study.

Figure 4 shows the induction time for methane hydrate in various concentrations of Potassium Oxalate Monohydrate (POM) solutions up to 2000 ppm, with the operating condition of 65 bar and 273.15 K. As shown in this Fig. 4 with the addition of POM solutions, the induction time for hydrate decreases up to certain POM concentration and then, increases. As illustrated in the figure with the addition of 250 ppm of POM solution into the system, the system experienced the highest reduction in induction time which is 5.34 h from 6.68 h. Then, at a high concentration of POM, induction time increases up to higher value than that of pure water.

The effect of POM concentration on the mole of methane consumed during hydrate growth is presented in the Fig. 5. As depicted from the Fig. 5, the addition of POM solution into the system does not have significant effect on the methane uptake. At a low concentration of POM, the methane uptake increase a bit but then, as the concentration of POM increases, the amount of methane uptake decreases to a very low value. Based on this finding and previous finding on the induction time for methane hydrate formation with the addition of POM, it seems that POM introduces more inhibition effect compared to promotion effect.

Figure 6 shows the effect of concentration of POM solutions on the apparent rate during the hydrate growth of methane hydrate. As depicted in the Fig. 6; the inclusion of POM has a very significant effect on the apparent rate of hydrate formation. At a low concentration of POM, the apparent rate increase but then, decreases with the increase of concentration of POM. This behaviour shows that, POM can be used as inhibitor at a high concentration of POM. Interestingly, at the 250 ppm of POM concentration, the apparent rate constant increases to nearly 7 times higher than that of pure water which is 0.72-0.108 h<sup>-1</sup>. Hence, from this, it can be concluded that, POM is good as a low dosage hydrate promoter.

## CONCLUSION

Experimental data on the kinetic of formation of methane hydrate in deionised water at different initial pressure and methane hydrate in the presence of various concentrations of POM are presented. The effect of initial methane pressure and the effect of POM solution on the kinetic of formation of hydrate is discussed. It can be concluded that the induction time for methane hydrate formation is lowered with the presence of POM in the system and it is concentration dependant. Besides that,

the methane consumed during gas hydrate formation and the apparent rate constant is found to be higher for methane hydrate in presence of POM when used at a low concentration of that POM. These results suggested that POM can be used as a low dosage promoter for gas hydrate based processes to improve the performance of these processes. Besides that, these results also show that POM can be used as inhibitor with high concentration of POM as its value is higher than that of pure water when used it is used in high concentration.

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