Effects of Mixed Surfactants on Methane Hydrate Formation and Dissociation

Katipot Inkong[a], Pramoch Rangsunvigit[a,*], Santi Kulprathipanja[b]

[a]The Petroleum and Petrochemical College, Chulalongkorn University, 254 Soi Chulalongkorn 12, Phayathai Rd.
 Pathumwan, Bangkok 10330, Thailand
[c]UOP, A Honeywell Company, Des Plaines, Illinois, 60017, USA
 Pramoch.r@chula.ac.th

Natural gas hydrates are ice-like crystalline and non-stoichiometric compounds formed by hydrogen bonds from water molecules when methane is trapped inside. Gas hydrates have received much attention not only as a new natural energy resource but also as a new means of natural gas storage and transportation. However, slow formation rate and stability of natural gas hydrates have been considered problems hindering the industrial applications. In this work, hydrate promoters, mixed MES and SDS, were investigated for hydrate formation and dissociation kinetic. The concentration of mixed surfactants were prepared at 0.5 mM MES/2 mMSDS, 1 mM MES/2mM SDS and 2mM MES/2mM SDS. The formation experiments were conducted in a batch reactor at 4 °C and 8 MPa. The results showed that all concentrations of mixed surfactant enhanced methane formation rate and methane consumption compared to pure water. The mixture of 0.5 mM MES and 2 mM SDS showed the highest methane consumption, while all concentrations of mixture showed the same rate of formation. The dissociation experiment was conducted after the formation with the driving force of 25 °C. The results showed that all promoters did not significantly affect the rate and methane recovery.

1. Introduction

Natural gas hydrates are ice-like crystalline compounds and non-stoichiometric compounds, which form when gaseous molecules such as methane, ethane, propane, nitrogen, and carbon dioxide are trapped inside cage formed by hydrogen bonds from water molecules. They are stable under high pressure and low temperature (Sloan and Koh, 2008). Natural gas hydrates are found in the permafrost region and in sediments of outer continental margins. There are three well-known structures of gas hydrates, including sI, sII, and sH (Demirbas, 2010).

In recent years, gas hydrates have received much attention not only as a new natural energy resource but also as a new mean of natural gas storage and transportation. At standard condition (STP), 150 - 180 m^3 of natural gas can be stored in 1 m^3 of hydrates (Saw et al., 2014). The ability to store a large amount of natural gas in the hydrate form makes a good candidate for the storage and safe transport of natural gas. However, slow formation rate and stability of natural gas hydrates have been considered problems hindering the industrial applications. Recently, many researchers have reported the effect of the promoter on the natural gas formation rate and it stability (Partoon and Javanmardi, 2013).

Surfactants are considered to be a chemical hydrate promoter, kinetic promoters, due to the fact that it can reduce the surface tension of gas-liquid interface, resulting in reduction of the diffusion resistance between two phases, and increase in the gas molecules solubility. Sun et al. (2004) investigated the effect of interfacial tension on the hydrate formation with sodium dodecyl sulfate (SDS). They found that the interfacial tension decreased with increasing pressure. Ganji et al. (2007) investigated the effect of different surfactants on methane hydrate formation. They found that all surfactants increased the hydrate formation rate and gas storage. There are reports that anionic surfactants promote gas hydrate formation effectively (Mandal and Laik, 2008). Zhong and Rogers (2000) reported that sodium dodecyl sulfate (SDS) increases the hydrate

formation of ethane and natural gas hydrate. They report that critical micelle concentration (CMC) of SDS solution was found at 242 ppm at hydrate formation condition. At concentration of SDS above the CMC, the hydrate formation rate increased by a factor of 700 compared to the system without any added surfactant. This hypothesis was supported by Lin et al. (2004). They reported that the maximum storage capacity of methane (170 V/V) was obtained at critical SDS concentration (650). In addition, they found that at concentration above the CMC, the rate of formation increased.). However, this hypothesis was disputed by Di Profio et al. (2005), who did not observe any micelle formation under hydrate formation conditions using SDS, including another anionic and cationic surfactants. This report was supported by Zhang et al. (2007). They concluded that the hydrate nucleation was influenced by the presence of additive (SDS) so that SDS micelle had little influence on the hydrate nucleation. However, SDS increased the hydrate nucleation rate and hydrate growth rate.

This work aims to improve the rate of hydrate formation and dissociation, and gas hydrate storage capacity transportation. Mixtures of surfactants, which were methyl ester sulfonate (MES) and SDS, were used to investigate their effects on the methane hydrate formation and dissociation kinetics.

2. Experimental Procedures

2.1 Chemical

Sodium dodecyl sulphate (SDS, 99.0 %) was purchased from Aldrich, Germany. Methyl ester sulfonate (MES, 99.7 %) supported by Lion Cooperation, Japanese. Deionized water was used for hydrate formation. Methane gas (CH_4, 99.99 %) was obtained from Linde Public Company, Thailand.

2.2 Experimental Apparatus

The schematic of the experimental apparatus is shown in Figure 1 (left side). The apparatus consisted of a high pressure crystallizer (CR) made by stainless steel cylindrical vessel with the internal volume of 57.28 cm^3. There was a reservoir (R) connected to the crystallizer for supplying and collecting gas. The crystallizer and reservoir were immersed in a cooling bath. Two pressure transducers were used to detect the pressure in the system with the range of 0 - 21 MPa with 0.13 % global error. Figure 1 (right side) shows the cross-section of the crystallizer. There were four K-type thermocouples placed in different location inside the crystallizer. Thermocouple number 1, 2 and 3 (T1, T2 and T3) were placed at the top, middle and bottom of the bed respectively. Moreover, thermocouple number 4 (T4) was placed at the bottom of the crystallizer. A Wisco data logger was connected to a computer to record the data.
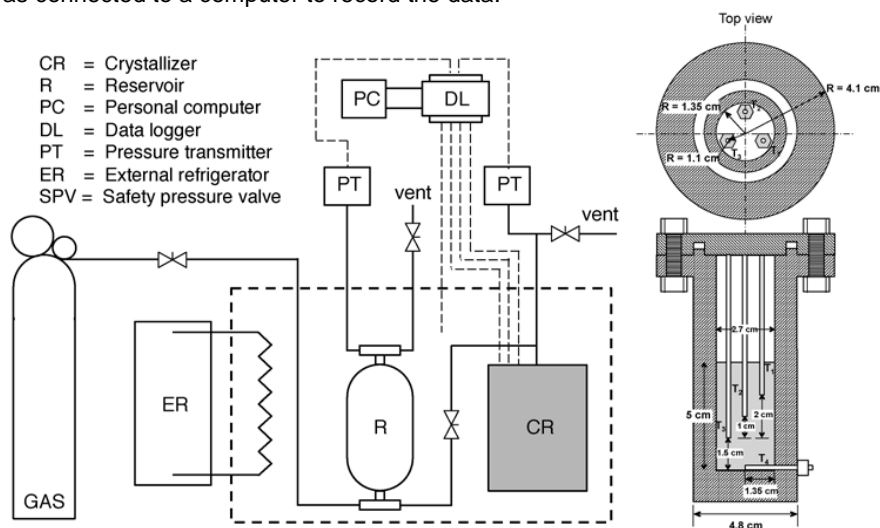

Figure 1: Schematic of experimental apparatus (left side) and cross-section of a crystallizer (right side)

2.3 Methane Hydrate Formation and Dissociation

The mixed surfactant solution was placed in the crystallizer. The amount of water added into the porous medium was calculated based on the porosity of the porous medium. The crystallizer was then pressurized to 0.5 MPa by the methane gas twice to ensure no more air bubble remain in the system. Methane gas was introduced into the crystallizer at the desired experimental condition (8 MPa at 4 °C). The data was recorded every 10 s. Pressure dropped in the crystallizer marked as the gas consumption during the methane

formation. The experiment was stopped when no significantly change in the pressure. The experiments were operated in the batch mode.

After the completion of methane hydrate formation experiment, the methane hydrate was dissociated by thermal stimulation. The gas released from the crystallizer was measured by the pressure transducer. The experiments were stopped when the pressure was constant at any given experimental temperature. At any given time, the total moles of gas in the system equal to the moles of gas at time zero. The methane consumption, water conversion and methane recovery were calculated based on the method outlined Siangsai et al. (2015).

3. Results and Discussions

3.1 Methane Hydrate Formation

The methane hydrate formation experiments were done at 4 °C and began with an initial pressure of 8 MPa. The summary of methane hydrate formation experimental conditions is shown in Table1 The experiments were carried out with three concentrations of mixed surfactants: MES/ SDS are 0.5 mM : 2 mM, 1 mM : 2 mM and 2 mM : 2 mM. The gas uptake and temperature profile during the hydrate formation at 4 °C and 8 MPa is shown in the Figure 2. The gas consumption during the hydrate formation can be characterized into two stages. The first stage involves the increase in a small amount of gas consumption resulted from hydrate nucleation. In the second stage, temperature spikes characterizing drastic hydrate growth can be observed in different thermocouple locations inside the crystallizer due to the exothermic reaction of methane formation. The gas uptake increases significantly during the event and continues to grow until it reaches the maximum formation. The competition of methane hydrate formation in each region can be observed in Figure 3. The results indicate that the first exothermic peak is detected from T1 region, which is located at gas phase. The second peak observed from T2, which is located at gas-liquid interface followed by T3 region, water phase, and T4 region, the bottom of crystallizer. These results can be explained by the fact that hydrates initially form at the gas/liquid interface at the crystallizer side wall and grow upwards until the upper edge. At the same time, the water level is decreased due to the water is delivered to grow the methane hydrates. After that, the methane-hydrates grow downward into the aqueous phase, which was also reported by Okutani et al. (2008) and Yoslim et al. (2010). The results in Table 1 show that the mixed anionic surfactants can promote the formation of methane hydrates formation. That is due to the mixed surfactants can reduce the surface tension of gas-liquid interface, resulting in decreased diffusion resistance between gas phase and liquid phase, increased gas solubility. Methane consumed and water conversion to hydrates increase with decreasing concentration MES, while decreasing MES concentration decreases the induction time.
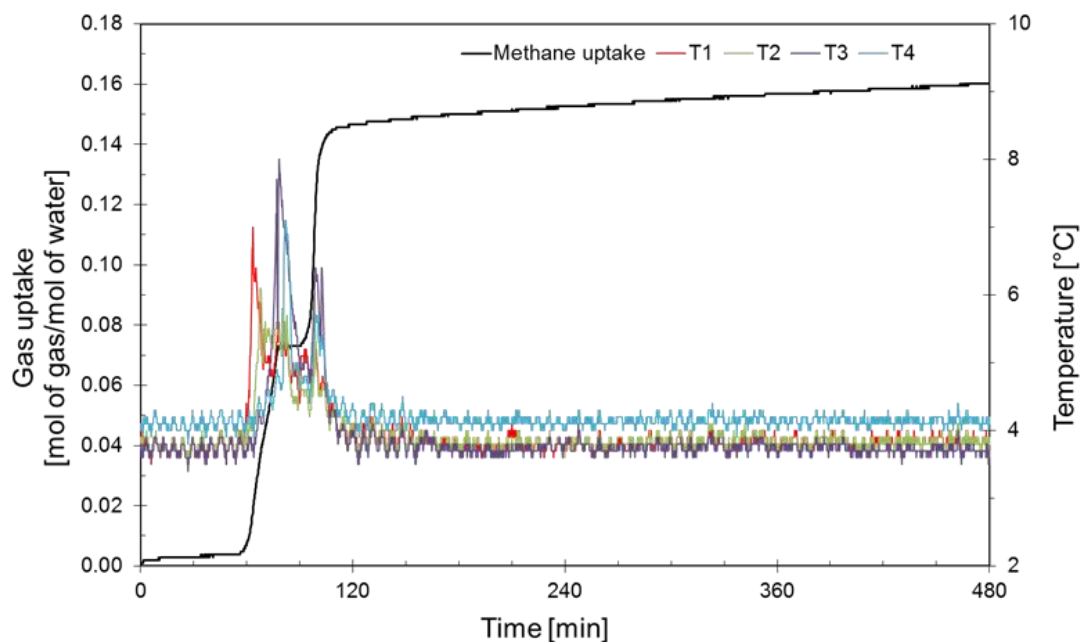

Figure 2: Methane hydrate formation at 8 MPa and 4°C in the presence of 0.5 mM MES + 2 mM SDS

Table 1: Methane hydrate formation experimental conditions at 4 °C

Exp. No.	Induction time (min)	Exp. duration dime (h)	CH$_4$ consumed (mol/mole H$_2$O)	Water conversion to hydrate (mol%)
0.5 mM MES + 2mM SDS				
1	13.30	9.7	0.1950	99.70
2	50.17	8.23	0.1667	86.31
3	12.33	9.7	0.1925	99.70
		Average	0.1796±0.0182	95.2367±7.73
1 mM MES + 2mM SDS				
1	24.17	8.03	0.1869	96.80
2	62.83	8.35	0.1807	93.62
3	26.33	7.24	0.1778	92.12
		Average	0.1818±0.0046	94.18±2.39
2 mM MES + 2 mM SDS				
1	44.50	9.77	0.1626	84.29
2	51.00	9.92	0.1621	84.02
3	476.17	15.83	0.1917	99.34
		Average	0.1721±0.0169	89.2167±8.77

3.2 Methane Hydrate Dissociation

The dissociation experiment starts after the formation of gas hydrate completes. Thermal stimulation to 25 °C was used to dissociate the hydrate formation in this research. Figure 2 shows gas methane released and temperature profile during the dissociation experiment in the presence of 0.5 mM MES + 2 mM SDS. The temperature of the cooling water (T$_{water}$) increased, causing the heat transfer between the external heater (water) and inside the crystallizer. Consequently, the temperature in the crystallizer is increased. When the temperature in the crystallizer crosses the hydrate phase equilibrium, the methane hydrate is released (endothermic process). At this point, the temperature is called dissociation temperature (T$_d$), which represents the point on methane hydrate equilibrium curve. The amount of methane released increases until reaching the plateau after the temperature crosses T$_d$. In addition, the thermocouples at different positions in the crystallizer indicate that all methane hydrate formation stars to dissociate at the same temperature. However, the dissociation completes when the temperature of all the thermocouple reaches the set point temperature (25 °C).

Table 2 summarizes the methane hydrate dissociation experimental conditions at the temperature driving force (ΔT) of 21 °C. The dissociation temperature of all the experiments is not significantly different, 6.3 - 7.2 °C. The final amount of methane released of all experiment is in the range between 82.2 - 94.4 %. Some methane gas still remains in the water, and it is not recovered as reported by Linga et al. (2009). The results show that all mixed surfactants in the dissociation experiment does not affect the dissociation temperature, CH$_4$ released, and CH$_4$ recovery at the same temperature driving force.

Table 2: Methane hydrate dissociation experimental conditions in the system with driving force 21 °C

Exp. No.	Dissociation temperature, T$_d$[b] [°C]	CH$_4$ released [mol/mol of H$_2$O]	CH$_4$ recovery [mol%]
0.5 mM MES + 2 mM SDS			
1	6.3	0.1552	95.75
2	6.5	0.1333	82.25
3	6.8	0.1754	91.52
	Average	0.1546±0.02105	89.84±6.91
1 mM MES + 2 mM SDS			
1	6.6	0.1634	87.47
2	6.8	0.1674	94.16
3	6.5	0.1569	86.84
	Average	0.1625±0.0053	89.49±4.06
2 mM MES + 2mM SDS			
1	6.3	0.1656	86.05
2	7.2	0.1443	86.59
3	6.9	0.1552	87.37
	Average	0.1552±0.6636	86.67±0.66

4. Conclusion

The effect of mixed surfactants on the hydrate formation and dissociation were demonstrated with the presence of 0.5 mM MES/2 mM SDS, 1mM MES/2 mM SDS and 2mM MES/2 mM SDS at 8 MPa and 4 °C in the quiescent condition. The result showed that the methane hydrate formation rate, induction time, and methane consumed were enhanced when compared to pure water. For the methane hydrate dissociation, the different concentrations of mixed surfactants did not significantly affect the rate and methane recovery.
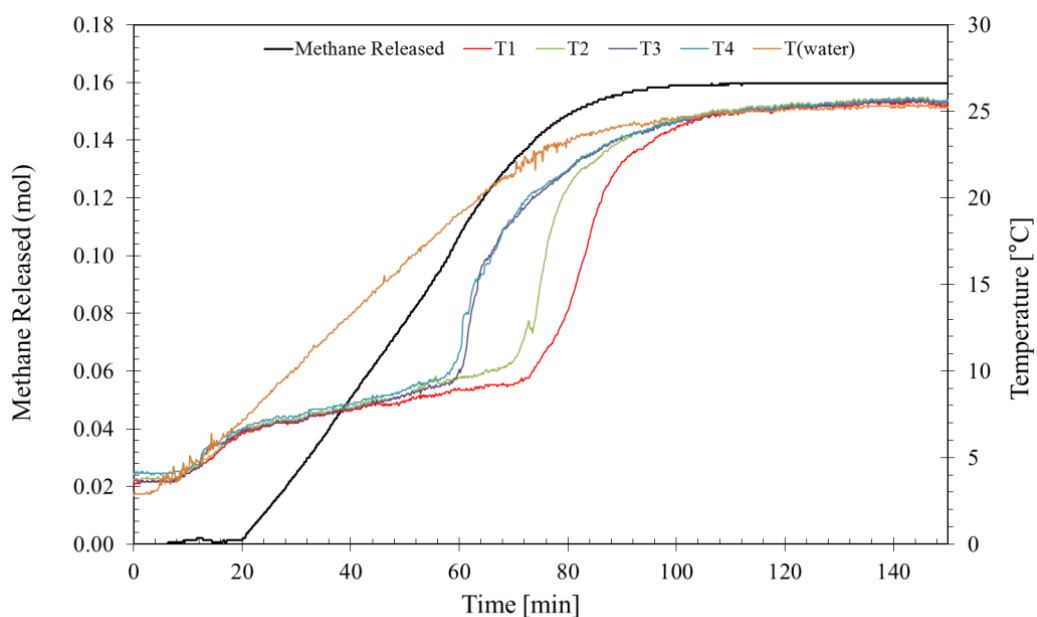
Figure 2: Methane hydrate dissociation in the presence of 0.5 mM MES + 2 mM SDS

References

Di Profio P., Arca S., Germani R., Savelli G., 2005, Surfactant promoting effects on clathrate hydrate formation: are micelles really involved?. Chemical Engineering Science, 60, 4141-4145.

Demirbas A., 2010, Methane hydrates as potential energy resource: Part 1 – Importance, resource and recovery facilities. Energy Conversion and Management, 51, 1547-1561.

Ganji H., Manteghian M., Omidkhah M.R., Mofrad H.R., 2007, Effect of different surfactants on methane hydrate formation rate, stability and storage capacity. Fuel, 86,434-441.

Lin W., Chen G.J., Sun C.Y., Guo X.Q., Wu Z.K., Liang M.Y., Yang L.Y., 2004. Effect of surfactant on the formation and dissociation kinetic behavior of methane hydrate. Chemical Engineering Science, 59, 4449-4455.

Linga P., Haligva C., Nam S.C., Ripmeester J.A., Engeloz P., 2009, Recovery of methane from hydrate formed in a variable volume bed of silica sand particles. Energy and Fuels, 23, 5508-5516.

Luo H., Sun C.Y., Peng B.Z., Chen G.J., 2006. Solubility of ethylene in aqueous solution of sodium dodecyl sulfate at ambient temperature and near the hydrate formation region. Journal of Colloid and Interface Science. 298, 952-956.

Mandal A., Laik S., 2008, Effect of the promoter on gas hydrate formation and dissociation, Energy and Fuels, 22, 2527-2532.

Okutani K., Kuwabara Y, Mori Y.H., 2008, Surfactant effects on hydrate formation in an unstirred gas/liquid system: An experimental study using methane and sodium alkyl sulfates, Chemical Engineering Science, 63, 183-194.

Partoon, B., Javanmardi, J., 2013, Effect of mixed thermodynamic and kinetic hydrate promoters on methane hydrate phase boundary and formation kinetics, Journal of Chemical & Engineering Data, 58, 501-509.

Siangsai A., Rangsunvigit P., Kitiyanan B., Kulprathipanja S., Linga P., 2015, Investigation on the roles of activated carbon particle sizes on methane hydrate formation and dissociation. Chemical Engineering Science, 126, 383-389.

Saw V.K., Gudala M., Udayabhanu G., Mandal A., Laik S., 2014, Kinetics of methane hydrate formation and its dissociation in presence of non-ionic surfactant Tergitol, Journal of Unconventional Oil and Gas Resources, 6, 54-59.

Sloan E.D., Koh C.A., 2008, Clathrate hydrates of natural gases, 3rd ed., CRC Press, Boca Raton, USA.

Sun C.Y., Chen G.J., Yang L.Y., 2004. Interfacial tension of methane + water with surfactant near the hydrate formation conditions. Journal of Chemical & Engineering Data, 49, 1023-1025.

Yoslim J., Linga P., Englezos P., 2010, Effects of different anionic surfactants on methane hydrate formation, Chemical Engineering Science, 137, 896-903.

Zhang J.S., Lee S., Lee J.W., 2007, Kinetics of methane hydrate formation from SDS solution, Industrial & Engineering Chemistry Research, 46, 6353-6359.

Zhong Y., Rogers R.E., 2000. Surfactant effects on gas hydrate formation. Chemical Engineering Science, 55, 4175-4187.