Title: Methane Gas Hydrate Kinetics with Mixtures of Sodium Dodecyl Sulfate and Tetrabutylammonium Bromide

Jean-Sébastien Renault-Crispo[1], *Phillip Servio*[1,*]

[1] Department of Chemical Engineering, McGill University, Montréal, Québec, Canada.

* Corresponding author's email: phillip.servio@mcgill.ca

Tel.: +15143981026

Fax: +15143986678

Postal address:

Room 3060, Wong Building

3610 University Street,

Montréal, Québec,

Canada, H3A 0C5

ABSTRACT

The effect of combining a thermodynamic promoter, tetrabutylammonium bromide (TBAB) with a kinetic promoter, sodium dodecyl sulfate (SDS) to a methane clathrate system was investigated. Kinetic growth experiments were conducted in a semi-batch stirred tank crystallizer at driving forces of 1500 kPa using a range of 100 to 1500 ppm SDS and 200 to 200 000 ppm TBAB. Solutions containing low concentrations of TBAB in water reduced methane hydrate growth rates up to 55 % for 1250 ppm TBAB compared to pure water. Solutions containing 900 ppm SDS in water enhanced the growth rate by 880 % compared to pure water. Solutions were then tested combining both promoters. The gradual addition of SDS from concentrations between 100 to 1250 ppm to low-concentration TBAB systems between 200 to 1250 ppm was initially found to reduce growth kinetics, but eventually increased the growth rates once a threshold SDS concentration was reached. In all cases, the promoting effect of SDS was more pronounced in the absence of the TBAB. The growth kinetics of systems containing 5 and 20 wt% TBAB also followed a similar inhibition-promotion trend with SDS concentration. An increase of 177 % in gas consumption rate was observed when 1500 ppm SDS was added to the 20 wt% TBAB clathrate system. This work demonstrates that SDS can be added to a TBAB-water-methane system to enhance gas consumption rates, but care must be taken to ensure that the concentration of the additives places the system in a promotion regime.

KEYWORDS

Gas hydrates; Growth rate; Kinetics; Tetrabutylammonium bromide; Sodium dodecyl sulfate

INTRODUCTION

Gas hydrates are solid inclusion compounds formed from the combination of water and gas molecules at high pressures and low temperatures. The solid phase consists of a host lattice of hydrogen-bonded water molecules that encage guest gas molecules, such as methane, carbon dioxide and propane.[1] Gas hydrate formation is problematic in oil and gas transmission lines during deep-water production and recovery.[2] Prevention and mitigation is essential to ensuring a continuous and safe fluid flow within pipelines and facilities. On the other hand, gas hydrates are considered a potential large-scale energy resource. They are found in enormous natural deposits in artic regions under the permafrost and in oceanic sediments along the continental margins.[3] Recognizing the immense potential energy resource that natural methane hydrates offer, the Methane Hydrate Research and Development Act was enacted by the United States Congress in the year 2000 to evaluate the feasibility of their extraction and use.[4] Correspondingly, Japan[5] has recently launched a research program for a methane hydrate exploratory drilling project, and India and China have invested into methane hydrate research and development programs for the possible recovery of natural deposits.[6]

More recently, gas hydrates have also been studied for other technological applications that include storage and transportation of natural gas and hydrogen.[7; 8] The use of gas hydrate pellets could be viable for remote natural gas recovery projects where production is too expensive for a pipeline and installing a liquefied natural gas plant is not economically viable.[9] The gas hydrate pellet application is near commercialization, with current reports now focusing on optimization of production efficiency, as can be seen in the pilot-scale project in Japan.[10] Another relevant application is the use of gas hydrates in separation processes such as flue gases, where carbon dioxide can be preferentially captured while excluding nitrogen and other benign molecules.[11-15] Collectively, each of these applications is made possible by the high storage capacity of gas hydrates. For instance, one cubic meter of methane hydrate can release up to 160 cubic meters of methane gas (at STP).[16] At the present time, the relatively severe conditions required for formation, the slow hydrate growth kinetics and the lack of scalability studies stand as the most significant barriers to the large-scale development of the described technologies.[17]

One method to facilitate the formation conditions of gas hydrates involves the use of thermodynamic promoters. These additives shift the phase equilibrium to more energetically favourable conditions, such as lower pressures and higher temperatures. One class of molecules that are effective thermodynamic promoters are quaternary ammonium salts. These molecules form a semi-clathrate structure with water by incorporating themselves into the water lattice, helping to stabilize the crystal structure and thereby significantly lowering the thermodynamic conditions required for formation. Quaternary ammonium salts usually have their cationic group occupying the interior of the cages as guest molecules, and their anionic group participating in the cage skeleton alongside water. The tetrabutylammonium bromide (TBAB) salt is the most common semi-clathrate-forming thermodynamic promoter, mainly due to its commercial availability and that it can form a hydrate phase at temperatures of up to 12.4 °C and at atmospheric pressure.[18; 19] Research in the field of semi-clathrates has generally focused on the thermodynamics of TBAB hydrates, specifically the equilibrium temperatures, pressures and TBAB liquid concentrations with single and multiple guest gases.[20-23] Li et al.[24] investigated the use of gas hydrates for separation of carbon dioxide from flue gases using TBAB hydrates. They demonstrated the capability of removing CO_2, and that TBAB accelerated gas hydrate growth rates and diminished induction time. Another study showed that a 40-45 wt% TBAB solution may be a promising cold storage material for air conditioning systems due to its high phase change temperature and its improved overall conversion of liquid to gas hydrate.[25] A study that sparked interest for this report was completed by Nguyen et al.[26] where looked at the influence of a range of TBAB concentrations (0.025 to 3 wt%) on gas uptake during the formation of CO_2 gas hydrates. They noticed that low concentrations of TBAB inhibited growth kinetics, where a minimum growth rate was observed at 0.125 wt% TBAB. Considering that TBAB is meant to facilitate gas hydrate formation, this peculiar result demonstrates that while gas hydrates may be easier to form in the presence of a thermodynamic promoter, the ensuing growth kinetics may be reduced. Using Sum Frequency Generated vibrational spectroscopy, Attenuated Total Reflectance Fourier Transform Infrared and molecular dynamic simulations, Nguyen et al. concluded that the surface adsorption of TBAB at the gas-water interface gave rise to the unexpected decrease in growth rates observed at dilute TBAB concentrations, making it more difficult for the gas to enter the liquid phase.

Slow hydrate growth kinetics can be overcome using kinetic promoter molecules. Surfactants were initially shown to enhance hydrate growth by Kutergin et al. [27] and Kalogerakis et al.[28] It was shown that the use of 242 ppm of the surfactant sodium dodecyl sulfate (SDS) increased hydrate growth rates up to 700 times compared to pure water in a quiescent system.[29] SDS and other types of surfactants also increased gas storage capacity by converting more of the available water into solid hydrate.[30; 31] In stirred systems, SDS promoted growth rate by a factor of nearly 5 compared to a pure water system.[32] An increasing sigmoidal trend was observed between SDS concentration and growth rate, with a maximum plateau reached around 575 ppm SDS.[32] In a review on the use of surfactants for gas hydrate promotion, Kumar et al.[33] reported that systems with added surfactants show reduced induction times, increased hydrate growth rates and increased conversion of water to hydrate (nearing unity). They noted that the promotion mechanism may not be directly linked to micelle formation, as the concentrations used are well below the critical micelle concentration (CMC) of 2278 ppm.[34; 35] Rather, they offered that the presence of surfactants reduces the vapour-liquid surface tension. This enhances the mass transfer across the vapour-liquid interface and also changes hydrate morphology, both of which increases the surface area for gas-water interaction. It is also suggested that the presence of surfactants promotes hydrate formation and growth by both preserving the gas-liquid interface and preventing hydrate agglomeration.[36] Ando et al.[37] have also observed no difference in gas consumption rate and hydrate conversion at below and above CMC for three different surfactants, further solidifying theory that micelles do not affect hydrate formation.

Finally, the idea of combining thermodynamic and kinetic additives has sparked renewed interest for gas hydrate promotion (and inhibition) in hopes of improving efficiencies through synergistic effects. Kakati et al.[38] investigated the effect of adding L-tyrosine (a thermodynamic inhibitor) and NaCl (a thermodynamic inhibitor) to Polyvinylpryvolidone (PVP) (a kinetic inhibitor), and the resulting impact on natural gas hydrate formation. The combination of these three compounds, two thermodynamic inhibitors and one kinetic inhibitor, resulted in an enhanced inhibition strength where a decrease in gas consumption rate of up to 27 % was observed compared to a pure water system. A synergistic effect in decreasing crystal growth rate was also seen by combining three thermodynamic inhibitors (PEG, PAM, HEC) with a kinetic inhibitor (PVP).[39] It was even suggested that a ternary solution was a better selection than a binary solution for inhibition purposes.

Mech et al.[40] combined different thermodynamic promoters (THF and TBAB) with thermodynamic inhibitors (NaCl, methanol, ethylene glycol), and an unexpected promotion effect was observed. A ternary mixture of 0.5 wt% THF, 10 wt% TBAB, and 10 wt% ethylene glycol in water shifted the equilibrium line to the right (promotion) in a manner greater than a binary mixture of 0.5 wt% THF and 10 wt% TBAB in water. However, it is important to note that the difference in equilibrium temperature was only 0.19 K, which is a weak thermodynamic promoter effect.

The combination of two kinetic promoters has also been studied in the past. Ganji et al.[41] added 300 ppm of xanthan to a 500 ppm SDS solution and observed a lower hydrate dissociation rate, which can be advantageous for storage and transportation applications. Another study looked at the behaviour of SDS on two different hydrate systems: cyclopentane and TBAB.[42] They concluded that the headgroup of SDS, DS-, adsorbs via hydrophobic forces to the surface of the hydrate. The presence of the Br- ion in the TBAB systems may compete with DS- for the adsorption on the hydrate surface, but DS- is reported to have a stronger affinity for the hydrate surface.[42] Recently, Brown et al.[43] studied the effect of combining different chemicals on the cyclopentane hydrate. They suggested that a mixture of dispersant, dodecylbenzenesulfonic acid, and kinetic hydrate inhibitor, polyvinylcaprolactam (PVCap), would make the cohesion forces between hydrate particles higher than the individual chemicals. However, a mixture of PVCap and a quaternary ammonium salt, Arquad 2HT-75, would result in a cohesive-reducing effect between hydrate particles greater than either additive on their own. This is a strong example of how two different chemical combinations may work either antagonistically or synergistically on gas hydrate growth. Another report from Kakati et al.[44] described that combining a thermodynamic promoter, THF, with a kinetic promoter, SDS, results in a gas consumption rate increase with increasing SDS concentration. A more favourable equilibrium was achieved by combining TBAB with cyclopentane than either of these promoters alone.[45] Lastly, the growth kinetics of methane hydrate systems containing either THF or TBAB along with SDS was investigated.[46] The experiments were conducted with mixtures of 5 to 10 wt% TBAB, 0.5 to 1 wt% THF, and 600 to 1000 ppm SDS. The THF-SDS system showed a drastic increase in methane consumption rate compared to the TBAB-SDS system. Mech et al.[46] also observed a behaviour where gas consumption decreases over time after the initial hydrate formation (2 hours). This was attributed to the possible absorption of SDS micelles around the TBAB molecules. The TBAB semi-clathrate system was optimal for promotion using 5 wt% TBAB + 600 ppm SDS, promoting better than with more SDS (5 wt% TBAB + 1000 ppm SDS) or with more TBAB (10 wt% TBAB + 600 ppm SDS).

The objective of this study is to examine the kinetic effect of combining a common thermodynamic promoter, TBAB, with a common kinetic promoter, SDS, in a methane gas hydrate system. The concentration of TBAB was varied from 200 to 200 000 ppm (0.02 to 20 wt%) while the range for SDS concentration was 100 to 1500 ppm (0.01 to 0.15 wt%). To the best knowledge of the authors, this is the first time that these combinations of concentrations are used to study initial growth rates of methane hydrates. An antagonistic effect between these two compounds was observed for the first time. This study can contribute to scalability studies for the development of different gas hydrate applications such as gas separation that aim to enhance gas hydrate formation and provide a better understanding of the mechanisms behind these two promoters.

MATERIALS AND METHODS

Experimental Setup

The experimental apparatus consists of a 600 mL stainless steel reactor that is submerged in a temperature-controlled 20 % by volume ethylene glycol-water bath, as displayed in Figure 1. Two MM-DO6 magnetic stirrers from Pressure Product Industries are used to evenly mix both the reactor and the temperature-controlled bath. The reservoir gas tank is used to keep the reactor pressure constant during experiments by feeding gas through a Baumann 51000 control valve. The valve receives a signal based on the difference in pressure between the reactor bias gas tank and the reactor. This signal increases when gas is consumed in the reactor and the control valve delivers gas to the reactor in response to this signal in order to maintain constant pressure. Pressures are monitored at three different locations using Rosemount pressure transducers configured to a span of 0 to 14 000 kPa for absolute pressure measurements and 0 to 2000 kPa for differential pressure measurements, with an accuracy of 0.065 % of the given span. Temperatures are recorded with RTD probes from Omega for the reactor liquid, reactor gas, and reservoir tank. Methane obtained from MEGS Inc. has a purity of 99.999 %. The water used is treated by a reverse-osmosis (RO) system with a 0.22 µm filter and has a conductivity of 10 µS and total organic content less than 10 ppm. The 50 wt% TBAB-water mixture is obtained from Sigma Aldrich and used to prepare the different TBAB mixtures used in this study. SDS is

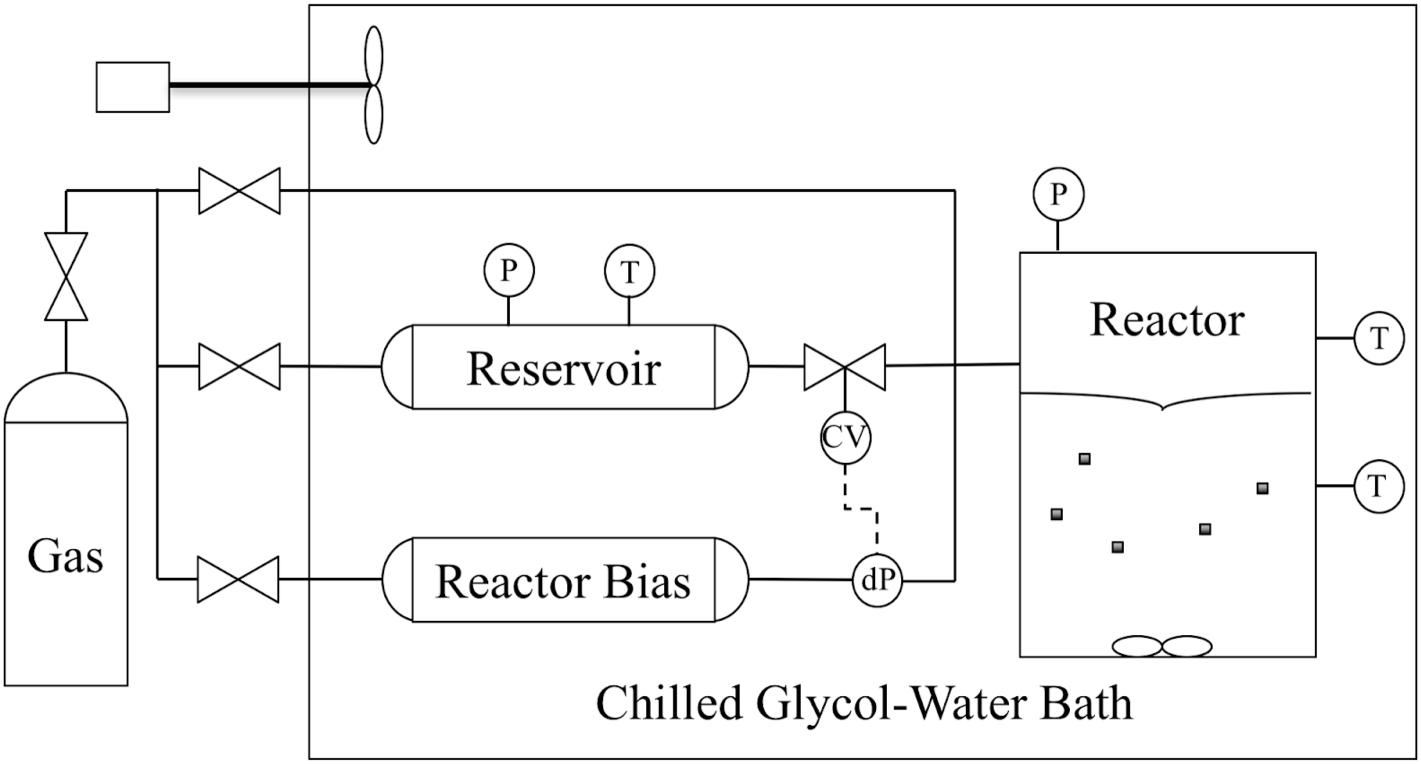

Figure 1: Experimental setup.

Experimental Procedure

Before starting experiments, the reactor was rinsed three times with 420 mL of RO water. The reactor was subsequently filled with 360 mL of the hydrate-forming liquid, which varied by experiment. The system temperature was fixed at the experimental temperature using the chiller to regulate the glycol bath. Once the liquid sample was loaded, the reactor was purged with methane gas three times by pressurizing to 1100 kPa followed by de-pressurizing to 110 kPa. The system was then pressurized to the experimental pressure based on the desired driving force. The reservoir and reactor bias gas tanks were filled with methane gas to a pressure 1000 kPa above the reactor value so as to provide a pressure differential for gas transfer during the kinetic runs. Once the reactor pressure and temperature stabilized, the data acquisition system and control valve were activated, and the magnetic stirrer inside the reactor was started. This begins the dissolution phase of a hydrate experiments that continues until the nucleation point, which is detected by a spike in bulk liquid temperature. Hydrate growth was recorded for at least 450 seconds beyond this point. Initial rates were used to avoid heat and mass transfer issues that arrive when the hydrate phase becomes a significant portion of the system. After the run, the data acquisition system and control valve were turned off and the reactor pressure was brought down to 110 kPa to allow the hydrates to dissociate. At this point, the experiment was either repeated to provide replicates or the reactor liquid was changed for experiments using a different mixture. Molar gas consumption rates, or hydrate growth rates, were calculated using the reservoir pressure and temperature data over the first 450 seconds of hydrate growth and converting this data to moles using the Trebble-Bishnoi equation of state.[47; 48] This equation of state was shown to adequately predict gas and liquid phases of water-gas systems.

RESULTS AND DISCUSSION

The analysis compares gas consumption rates without taking into account the role that induction time may have on growth rate, as the results were shown not to be a function of induction time as anticipated for systems with methane gas as the hydrate former.[49] Hence the gas consumption rates of each liquid mixture can be correctly compared in the analysis. At least three runs were performed for each liquid mixture. The average value is shown in the figures with a 95 % confidence interval (based on a t-test).

Pure SDS

Pure SDS runs were performed as a baseline to compare with literature values. Experiments were conducted at 2 °C and 4646 kPa, equivalent to about 1500 kPa driving force[50]. Verrett and Servio[32] demonstrated that the methane hydrate growth rate followed a sigmoidal trend with SDS concentration, where rates start to increase at SDS concentration of 150 ppm and reach a maximum around 575 ppm. The results from Figure 2 show the relative gas consumption rate change with SDS concentration for the current methane hydrate system compared to a pure methane-water system. This data supports the literature that an increase in gas consumption rate occurs between 100 ppm and 300 ppm[32]. Initially, SDS does not promote growth until a specific concentration is used (300 ppm in this case). However, the value of gas consumption rate did not plateau as clearly as it did in the study by Verrett and Servio,[32] but seemed to continue increasing after the 575 ppm mark. At 900 ppm, the growth rate enhancement was 880 % compared to pure water methane hydrates, while at 575 ppm it was 593

%. The authors believe that this slight variation in results is an effect of a different experimental setup, experimental procedure, and mixing speed. Furthermore, the complexity of hydrate growth in the presence of SDS could also contribute to different hydrodynamics. With the added surfactant, the liquid is seen to foam significantly and initial hydrate growth typically occurs along the walls of the reactor. The use of a metal stirring shaft that traverses the gas-liquid interface in Verrett and Servio[32] may also provide an extra surface for hydrates to grow. In this study, a magnetic stir bar situated at the bottom of the liquid was used to mix the system, possibly allowing for greater promotion. All these effects make it difficult to compare results between two different experimental setups in absolute terms, however the relative results are quite consistent.

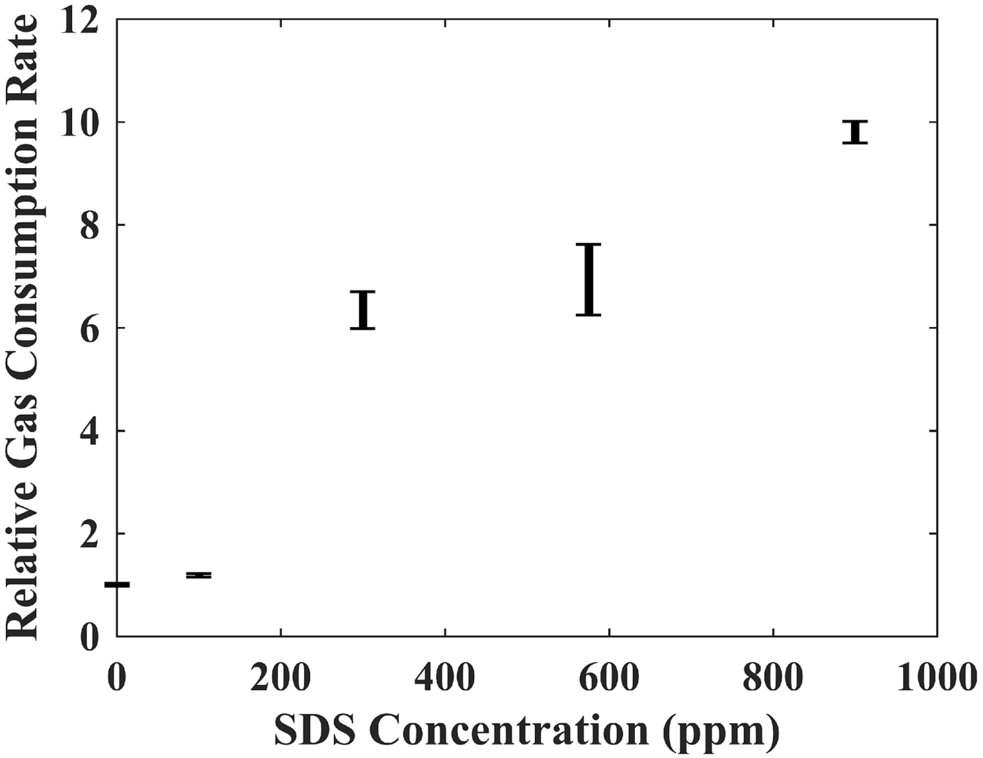

Figure 2: Relative methane gas consumption rate compared to pure water as a function of SDS concentration. Vertical error bars correspond to 95 % confidence intervals.

Pure TBAB at Low Concentrations

This section presents the results of low concentration TBAB (80 to 1250 ppm) and to the best knowledge of the authors, it is the first time this has been reported for a methane gas hydrate system. Once again, experiments were conducted at 2 °C and 4646 kPa, equivalent to a 1500 kPa driving force[50]. Equilibrium condition measurements were performed at the 1250 ppm TBAB concentration using experimental procedure found in Verrett et al.[23] It is important to note that the equilibrium pressure was found to be 77 kPa higher than pure water, corresponding to an unexpected small degree of thermodynamic inhibition. This means that the driving force for this concentration is approximately 5 % lower than the other concentrations (1423 kPa versus 1500 kPa). Nguyen et al.[26] have explained this inhibition at dilute TBAB concentration as a gas-water interface adsorption of TBAB that gives rise to inhibition at low concentration. The promotion effect of TBAB is not strong enough at these low concentrations to compensate for the inhibition. The equilibrium pressure for the other TBAB concentrations (80 to 575 ppm) were not found to be statistically different than pure water. Figure 3 displays the results for methane hydrate gas consumption rate with different concentrations of TBAB. It can be seen that gas consumption rates decrease with increasing TBAB concentrations. A 22 % decrease was observed for 575 ppm TBAB, and a 55 % reduction was seen for 1250 ppm TBAB. At 1250 ppm, the 5 % decrease in driving force cannot completely account for the 55 % inhibition detected since the other concentrations also decrease gas consumption rate but with no noticeable equilibrium change. At these low TBAB concentrations, TBAB acts as a kinetic inhibitor, in that it reduces the observed growth rates. However, the literature suggests that the advantage of using TBAB lies in its ability to be a thermodynamic promoter, which is not yet noticeable at these low concentrations. Nguyen et al.[26] also reported a decreasing trend with increasing TBAB concentration, similar to the one presented here, but in carbon dioxide gas hydrate systems. They indicated that gas uptake is at a minimum at 1250 ppm TBAB, and gas uptake will increase with either increasing or decreasing TBAB concentration from this point. It is important to note that they used the same pressure driving force for concentrations higher than 1250 ppm. At these levels of TBAB, the shift in equilibrium conditions becomes more significant, which makes it difficult to meaningfully compare growth rate results across TBAB concentrations. For instance, the equilibrium conditions at 5 wt% TBAB is significantly different than at 0.1250 wt% (1250 ppm).[23] It is for this reason that the results for higher concentrations of TBAB (> 1250 ppm) are addressed in a separate section and are not compared to the low concentration results in this article. This interesting promotion-inhibition effect from a same compound has also been observed for a well-known kinetic inhibitor, PVP. Ke at al.[51] showed that PVP at 50 and 100 ppm can have a promotive effect on nucleation rate at certain subcoolings, yet an inhibitory effect at other subcoolings. This illustrates the possibility of the opposing effects that a single additive may have on different aspects of a gas hydrate system.

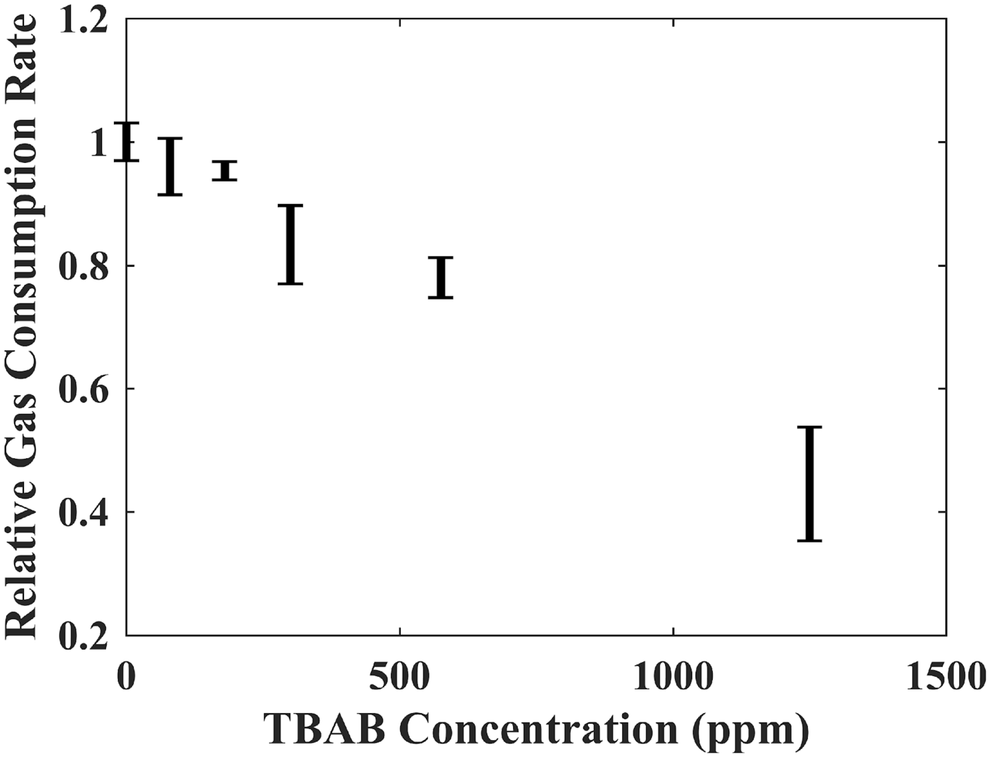

Figure 3: Relative methane gas consumption rate compared to pure water as a function of TBAB concentration. Vertical error bars correspond to 95 % confidence intervals.

Low Concentration TBAB with SDS

After noticing the decreasing trend in hydrate growth rate with TBAB concentrations up to 1250 ppm in the previous section, an investigation was conducted to examine whether the combination of the kinetic promoter SDS with the seemingly-inhibiting TBAB could improve the hydrate growth rate. Figure 4 shows the relative gas consumption rates (compared to pure water) of systems containing increasing SDS concentrations (100 to 1250 ppm) and three different concentrations of TBAB (200, 500, and 1250 ppm). Since the results are all normalized based on the pure water run, the different TBAB concentrations have a different growth rate at 0 ppm SDS, corresponding to the results of Figure 3. The absolute values of gas consumption rate are provided in Table 1. These experiments were also conducted at 2 °C and 4646 kPa, equivalent to a 1500 kPa driving force. At all TBAB concentrations (red, green and blue lines in Figure 4), a decrease in gas consumption rate compared to the baseline of no TBAB is observed at low SDS concentrations (lower than 400 ppm SDS). This means that when SDS is added in a small amount to a low concentration TBAB solution, an inhibition effect greater than the low concentration TBAB solution itself is detected. At 200 ppm TBAB, this inhibition occurs up to 200 ppm SDS, while at 500 and 1250 ppm TBAB, it is present up to 400 ppm SDS. A 64 % inhibition compared to the 500 ppm TBAB system (69 % inhibition compared to pure water) is observed when a solution of 500 ppm TBAB with 400 ppm SDS is used. Similarly, at 1250 ppm TBAB, a 43 % inhibition is seen when only 100 ppm of SDS is added. After this initial inhibition, the continued addition of SDS will eventually promote the gas consumption rate above its baseline of 0 ppm SDS. This transition happens earlier at lower TBAB concentrations, meaning that TBAB has an antagonistic effect on the promotion of SDS of methane hydrate growth. In the case where growth rate promotion is the main goal, the best solution would be one that does not contain TBAB as shown in Figure 4 where the black line (no TBAB) has the greatest values of gas consumption rate and does not change the thermodynamic equilibrium significantly.

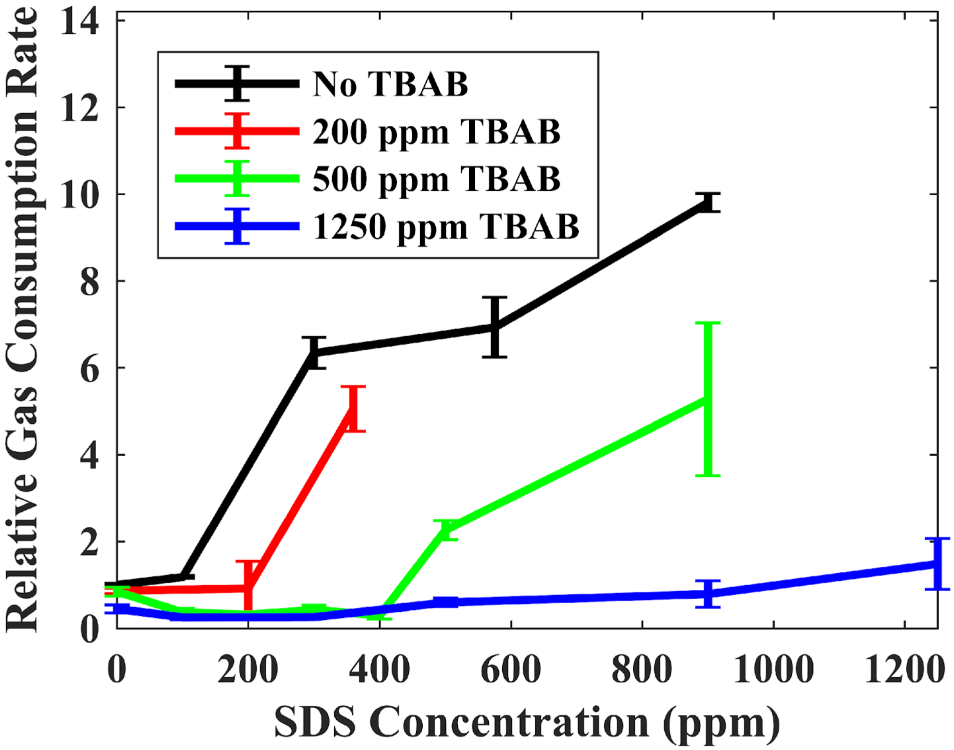

Figure 4: Relative methane gas consumption rate compared to pure water as a function of SDS concentration and four TBAB concentrations. Vertical error bars correspond to 95 % confidence intervals.

Table 1: Absolute methane gas consumption rate values for all mixtures of low concentration TBAB and SDS. Confidence intervals are omitted for clarity but can be found in Figure 4.

SDS Concentration (ppm)	TBAB concentration (ppm)	Average gas consumption rate * 1e6 (mol/s)	Relative to pure water
0	0	15.0	1
0	200	12.9	0.86
200	200	13.8	0.92
360	200	75.8	5.06
0	500	12.6	0.84
100	500	5.5	0.36
200	500	4.7	0.31
300	500	6.3	0.42
400	500	4.6	0.30
500	500	33.9	2.26
900	500	79.1	5.28
0	1250	6.7	0.45
100	1250	3.8	0.26
300	1250	3.9	0.26
500	1250	8.9	0.60
900	1250	11.8	0.79
1250	1250	22.2	1.48

Different hypotheses can be made with regards to why TBAB is inhibiting the effect of SDS on gas hydrate growth promotion. The presence of TBAB alter the critical micelle concentration (CMC) of SDS (2278 ppm),[35] possibly causing a change in the mechanism of hydrate growth promotion. It was shown by Mata et al.[35] that SDS exhibited a decrease in CMC with the addition of TBAB at 25 °C. About a tenfold decrease of CMC from 2278 ppm SDS at 0 ppm TBAB to 270 ppm SDS at 322 ppm TBAB was observed. Micelles may prevent SDS from kinetically promoting hydrate formation and thus the need for more SDS to do the same promotion effect. Additionally, other than the change in CMC, they report that the mixture of these compounds showed enhanced solubilization properties and a remarkable decrease in surface tension due to the increased interaction forces and thus binding ability of bulky tetrabutylammonium ion on NaDS. These concentration values are within the range at which the values of gas consumption rate start increasing in Figure 4, indicating the possibility of micelle formation which could be important to understanding how these two additives change the growth process. It is important to note that the reported CMC values were at 25 °C and that CMC is usually a complex function of temperature for surfactants. However, there is no direct evidence for or against micelle formation in aqueous TBAB and SDS mixtures at 2 °C, the experiments completed in this study. For pure aqueous SDS containing no other surfactants, micelles do not form at temperature lower than 8 °C[52]. Mohajeri et al. have shown that below 40 °C, another surfactant, polysorbate, had its CMC increase with decreasing temperature, a trend that was inversed at temperatures above 40 °C.[53] Morphology studies and CMC determination at hydrate conditions would bring valuable information on the effect of TBAB and SDS on the hydrate growth mechanism.

While lower concentration TBAB solution are less likely to be used because of the adverse effects shown, higher concentration TBAB solutions are still viable additives for their thermodynamic promotion ability, and promotion effects with the kinetic promoter SDS are still viable.

High Concentration TBAB with SDS

Kinetic results for 5 and 20 wt% TBAB with different SDS concentration can be found in Figure 5. Actual values for gas consumption rates can be found in Table 2. The gas consumption rates have been normalized to the 0 ppm SDS run in both the 5 and 20 wt% TBAB cases. Experiments for 5 wt% were completed at 10.2 °C and 3917 kPa, and 14.1 °C and 2935 kPa for the 20 wt%, both corresponding to a 1500 kPa driving force.[23] Both concentrations exhibit a decline in methane gas consumption rate at small concentrations of SDS (100 to 500 ppm). At concentrations above 500 ppm SDS, the systems start benefitting from the presence of higher concentration SDS and ultimately promote gas consumption rates relative to the 0 ppm SDS baseline. An increase of 177 % was observed for 1500 ppm SDS in a 20 wt% TBAB semi-clathrate system compared to 20 wt% TBAB alone. The transition of inhibition to promotion is found at a higher SDS concentration when 5 and 20 wt% TBAB is used compared to the lower TBAB concentrations in the previous section. The threshold concentration where the system transitions from inhibiting to promoting increases with increasing TBAB concentration in all cases. From Figure 4, 200 ppm TBAB only needed 360 ppm SDS to promote the methane gas consumption rate to 405 % while at 5 wt% TBAB and 500 ppm SDS, an inhibition of 34 % is still detected. The collective results at low and high concentrations of TBAB, with and without SDS, show that opposite effects can be observed with respect to hydrate growth rates, depending on the combination and concentration of the additives used. In the design of industrial applications where the TBAB-SDS semi-clathrate hydrate system is being considered, it is vital to be aware of the existence of this dual inhibition-promotion effect so that the desired effect is achieved.

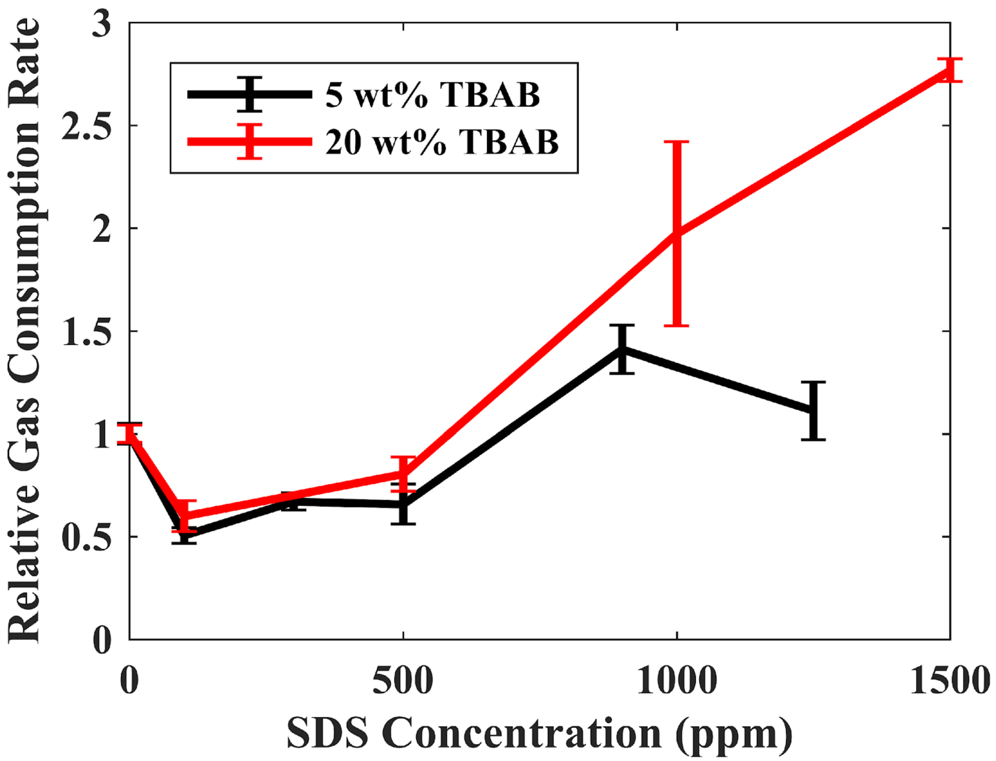

Figure 5: Relative methane gas consumption rate compared to 0 ppm SDS (pure TBAB) as a function of SDS concentration. Vertical error bars correspond to 95 % confidence intervals.

Table 2: Absolute methane gas consumption rate values for all mixtures of high concentration TBAB and SDS. Confidence intervals are omitted for clarity but can be found in Figure 5.

SDS Concentration (ppm)	TBAB concentration (wt%)	Average gas consumption rate * 1e6 (mol/s)	Relative to 0 ppm SDS
0	5	5.6	1.00
100	5	2.8	0.51
300	5	3.7	0.67
500	5	3.7	0.66
900	5	7.9	1.41
1250	5	6.2	1.11
0	20	4.8	1.00
100	20	2.9	0.60
500	20	3.9	0.80
1000	20	9.5	1.97
1500	20	13.4	2.76

CONCLUSION

An investigation into the addition of the kinetic promoter SDS to a TBAB-methane semi-clathrate system was undertaken over a range of 100 to 1500 ppm SDS and 200 to 200 000 ppm TBAB (0.02 to 20 wt%). The growth rates of methane hydrate systems containing only SDS were found to begin to increase at similar threshold values as reported in literature, but surpassed reported plateau values without tailing off. A growth rate enhancement of 880 % compared to pure water was observed at the highest concentration of SDS used (900 ppm). In methane hydrate systems containing low concentrations of the thermodynamic promoter TBAB (200 to 1250 ppm), hydrate growth was found to decrease monotonically as a function of TBAB concentration, reaching 55 % inhibition at 1250 ppm TBAB. The addition of 100 to 1250 ppm SDS to these 200 to 1250 ppm TBAB systems initially slowed hydrate growth to an even larger extent than just TBAB, but eventually promoted the growth rates once a threshold SDS concentration was reached. However, the promotion effect was more pronounced without the presence of TBAB. The formation kinetics of 5 and 20 wt% TBAB systems also followed a similar inhibition-promotion trend with increasing SDS concentration. An increase of 177 % in the gas consumption rate was recorded when 1500 ppm SDS was added to the 20 wt% TBAB clathrate system. In sum, SDS can be added to a TBAB-water-methane system to enhance gas consumption rates, but care must be taking to be above the threshold concentration of the inhibition-promotion effect.

ACKNOWLEDGMENTS

The authors are grateful to the Natural Sciences and Engineering Research Council of Canada (NSERC), les Fonds de recherche du Québec – Nature et technologies (FRQNT), the McGill Engineering Doctoral Award (MEDA) program, and the Department of Chemical Engineering of McGill University for financial support.

REFERENCES

[1] E. D. Sloan, C. A. Koh, *Clathrate hydrates of natural gases*, CRC Press, Boca Raton, FL **2008**.

[2] C. A. Koh, E. D. Sloan, A. K. Sum, D. T. Wu, *Annual Review of Chemical and Biomolecular Engineering*. **2011**, *2*. 237-257.

[3] T. Collett, J.-J. Bahk, R. Baker, R. Boswell, D. Divins, M. Frye, D. Goldberg, J. Husebø, C. Koh, M. Malone, M. Morell, G. Myers, C. Shipp, M. Torres, *Journal of Chemical & Engineering Data*. **2015**, *60*. 319-329.

[4] National Research Council, "Charting the future of methane hydrate research in the United States," in National Academies Press, Washington, D.C., (2004)

[5] K. Yamamoto, Y. Terao, T. Fujii, T. Ikawa, M. Seki, M. Matsuzawa, T. Kanno, "Operational overview of the first offshore production test of methane hydrates in the Eastern Nankai Trough," in Offshore Technology Conference(2014)

[6] T. M. Letcher, *Future Energy: Improved, Sustainable and Clean Options for our Planet*, 2nd Edition edition, **2014**.

[7] J. S. Gudmundsson, F. Hveding, A. Børrehaug, "Transport Or Natural Gas As Frozen Hydrate," in International Society of Offshore and Polar Engineers(1995)

[8] T. Sugahara, J. C. Haag, P. S. Prasad, A. A. Warntjes, E. D. Sloan, A. K. Sum, C. A. Koh, *Journal of the American Chemical Society*. **2009**, *131*. 14616-14617.

[9] J. S. Gudmundsson, V. Andersson, O. I. Levik, M. Mork, *Annals of the New York Academy of Sciences*. **2000**, *912*. 403-410.

[10] S. Watanabe, S. Takahashi, H. Mizubayashi, S. Murata, H. Murakami, "A demonstration project of NGH land transportation system," *Proceedings of the 6th international conference on gas hydrates*, **2008**.

[11] S.-P. Kang, H. Lee, *Environmental science & technology*. **2000**, *34*. 4397-4400.

[12] A. Eslamimanesh, A. H. Mohammadi, D. Richon, P. Naidoo, D. Ramjugernath, *The Journal of Chemical Thermodynamics*. **2012**, *46*. 62-71.

[13] Z. W. Ma, P. Zhang, H. S. Bao, S. Deng, *Renewable and Sustainable Energy Reviews*. **2016**, *53*. 1273-1302.

[14] I. Chatti, A. Delahaye, L. Fournaison, J.-P. Petitet, *Energy Conv. Manag.* **2005**, *46*. 1333-1343.

[15] P. Babu, P. Linga, R. Kumar, P. Englezos, *Energy*. **2015**, *85*. 261-279.

[16] M. Taylor, R. A. Dawe, S. Thomas, "Fire and Ice: Gas Hydrate Transportation - A Possibility for the Caribbean Region," in "SPE Latin American and Caribbean Petroleum Engineering Conference," Society of Petroleum Engineers, Port-of-Spain, Trinidad and Tobago, (2003)

[17] Z. Yin, Z. R. Chong, H. K. Tan, P. Linga, *Journal of Natural Gas Science and Engineering*. **2016**. 1362-1387.

[18] L. S. Aladko, Y. A. Dyadin, T. V. Rodionova, I. S. Terekhova, *Journal of Structural Chemistry Journal of Structural Chemistry*. **2002**, *43*. 990-994.

[19] W. Shimada, M. Shiro, H. Kondo, S. Takeya, H. Oyama, T. Ebinuma, H. Narita, *Acta Crystallographica Section C*. **2005**, *61*. o65-o66.

[20] M. Arjmandi, A. Chapoy, B. Tohidi, *Journal of Chemical & Engineering Data*. **2007**, *52*. 2153-2158.

[21] A. Bouchemoua, P. Brantuas, J.-M. Herri, "Equilibrium data of CO2-based semi-clathrates from quaternary ammonium solutions," *7th International Conference on Gas Hydrates (ICGH 2011)*, Edimbourg, United Kingdom, 2011-07-17 **2011**.

[22] Z.-G. Sun, L. Sun, *Journal of Chemical & Engineering Data*. **2010**, *55*. 3538-3541.

[23] J. Verrett, J.-S. Renault-Crispo, P. Servio, *Fluid Phase Equilibria*. **2015**, *388*. 160-168.

[24] X.-S. Li, Z.-M. Xia, Z.-Y. Chen, K.-F. Yan, G. Li, H.-J. Wu, *Industrial & Engineering Chemistry Research*. **2010**, *49*. 11614-11619.

[25] B. Mahmoudi, P. Naeiji, F. Varaminian, *Journal of Molecular Liquids*. **2016**, *214*. 96-100.

[26] N. N. Nguyen, A. V. Nguyen, K. T. Nguyen, L. Rintoul, L. X. Dang, *Fuel*. **2016**, *185*. 517-523.

[27] O. B. Kutergin, V. P. Melnikov, A. N. Nesterov, *Doklady Akademii Nauk*. **1992**, *v. 323*. 549-553.

[28] N. Kalogerakis, A. K. M. Jamaluddin, P. D. Dholabhai, P. R. Bishnoi, "Effect of Surfactants on Hydrate Formation Kinetics," in Society of Petroleum Engineers(1993)

[29] Y. Zhong, R. E. Rogers, *Chemical Engineering Science*. **2000**, *55*. 4175-4187.

[30] Z. Sun, R. Wang, R. Ma, K. Guo, S. Fan, *International Journal of Energy Research*. **2003**, *27*. 747-756.

[31] K. Okutani, Y. Kuwabara, Y. H. Mori, *Chemical Engineering Science*. **2008**, *63*. 183-194.

[32] J. Verrett, P. Servio, *Industrial & Engineering Chemistry Research*. **2012**, *51*. 13144-13149.

[33] A. Kumar, G. Bhattacharjee, B. D. Kulkarni, R. Kumar, *Industrial & Engineering Chemistry Research*. **2015**, *54*. 12217-12232.

[34] P. Di Profio, S. Arca, R. Germani, G. Savelli, *Chemical Engineering Science*. **2005**, *60*. 4141-4145.

[35] J. Mata, D. Varade, G. Ghosh, P. Bahadur, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. **2004**, *245*. 69-73.

[36] M. Mitarai, M. Kishimoto, D. Suh, R. Ohmura, *Crystal Growth & Design*. **2015**, *15*. 812-821.

[37] N. Ando, Y. Kuwabara, Y. H. Mori, *Chemical Engineering Science*. **2012**, *73*. 79-85.

[38] H. Kakati, A. Mandal, S. Laik, *Journal of Natural Gas Science and Engineering*. **2016**, *34*. 1361-1368.

[39] E. F. Jokandan, P. Naeiji, F. Varaminian, *Journal of Natural Gas Science and Engineering*. **2016**, *29*. 15-20.

[40] D. Mech, J. S. Sangwai, *Journal of Chemical & Engineering Data*. **2016**, *61*. 3607-3617.

[41] H. Ganji, M. Manteghian, H. Rahimi Mofrad, *Fuel Processing Technology*. **2007**, *88*. 891-895.

[42] C. Lo, J. S. Zhang, P. Somasundaran, S. Lu, A. Couzis, J. W. Lee, *Langmuir*. **2008**, *24*. 12723-12726.

[43] E. P. Brown, C. A. Koh, *Energy & Fuels*. **2016**, *30*. 8065-8071.

[44] H. Kakati, A. Mandal, S. Laik, *Journal of Energy Chemistry*. **2016**, *25*. 409-417.

[45] F. Tzirakis, P. Stringari, N. von Solms, C. Coquelet, G. Kontogeorgis, *Fluid Phase Equilibria*. **2016**, *408*. 0e247.

[46] D. Mech, P. Gupta, J. S. Sangwai, *Journal of Natural Gas Science and Engineering*. **2016**, *35, Part B*. 1519-1534.

[47] M. A. Trebble, P. R. Bishnoi, *Fluid Phase Equilibria*. **1988**, *40*. 1-21.

[48] M. A. Trebble, P. R. Bishnoi, *Fluid Phase Equilibria*. **1987**, *35*. 1-18.

[49] J.-S. Renault-Crispo, P. Servio, *Journal of Natural Gas Science and Engineering*. **2017**.

[50] T. Nakamura, T. Makino, T. Sugahara, K. Ohgaki, *Chemical Engineering Science*. **2003**, *58*. 269-273.

[51] W. Ke, T. M. Svartaas, J. T. Kvaløy, B. R. Kosberg, *Energy & Fuels*. **2016**, *30*. 7646-7655.

[52] K. Watanabe, S. Imai, Y. H. Mori, *Chemical Engineering Science*. **2005**, *60*. 4846-4857.

[53] E. Mohajeri, G. D. Noudeh, *E-Journal of Chemistry*. **2012**, *9*.