INFLUENCE OF MELTING RATE ON THE DISSOCIATION OF GAS HYDRATES WITH THE KINETIC INHIBITOR PVCAP PRESENT

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ABSTRACT

The kinetic inhibitor Poly Vinyl Caprolactam (PVCap) was added as a kinetic inhibitor to the gas-water system. Different hydrate formers were used in order to obtain formation of the different hydrate structures (sI, sII and sH). All hydrate structures were formed with PVCap. The effect of applying different melting rates was investigated. The isochoric technique was used to obtain dissociation temperatures and corresponding pressures. The melting rate was found to be a parameter influencial for the dissociation temperature. Even for very slow melting rates such as 0.0125 Kelvin per hour, the final dissociation temperature was significantly higher that the dissociation temperature for the corresponding non-inhibited system.

Keywords: gas hydrates, dissociation, melting rate, kinetic inhibitors, PVCap

NOMENCLATURE

$\delta T/\delta t$: Heating rate	[°C/h]
M_w: Average molecular weight	[Dalton]
ΔT: Displacement of dissociation temp.	[°C]
T_{exp}: measured equilibrium temp.	[°C]
T_{CSMHYD}: predicted equilibrium temp.	[°C]

INTRODUCTION

Gas hydrates are non-stoichiometric inclusion compounds that are formed by the physically stable interaction between water and relatively small guest molecules occupying the hydrogen-bonded framework constituted by the water molecules. This framework constitutes cages, which are stabilized due to the inclusion of guest molecules. They form different structures known as structure I (sI), structure II (sII) and structure H (sH). sI and sII are cubic structures while sH is a hexagonal structure. The ratio of small to large cages varies for the three structures, and the cages are constituted by tetragonal, pentagonal and hexagonal networks of water molecules according to Table1.1.

	Cavity Structure				
	5^{12}	$5^{12}6^2$	$5^{12}6^4$	$4^35^66^3$	$5^{12}6^8$
s I	2	6			
s II	16		8		
s H	3			2	1

Table 1. Overview of the cavities that are incorporated into the various hydrate structures.

Hydrates may form in the presence of low temperature and high pressure. Occurrence of hydrate formation can lead to great problems for the hydrocarbon transportation lines, where hydrates can cause complete blockage of the pipe. Such a situation is especially a relevant scenario when there is a shut-down situation, where one is entering into the pressure and temperature region for hydrate formation. Various mitigation strategies have evolved, which are classified either as thermodynamic inhibitor methods or kinetic inhibition methods. Thermodynamic methods use great amounts of methanol and glycol, up to 50% of the water phase. This makes the procedure a

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costly one. The kinetic inhibition methods are based on injection of watersoluble polymer-based chemicals. This method only requires an inhibitor amount of up to 0.3 weight percent of the water phase, and can thus act as a cost saving alternative. The kinetic inhibitors do not prevent the formation of hydrates, but delay hydrate nucleation and growth. It is believed that the kinetic inhibitors raise the surface energy of the pre-nucleation aggregates, thus increasing the activation energy barrier for nuclei formation.

EXPERIMENTAL PROCEDURE AND DESCRIPTION

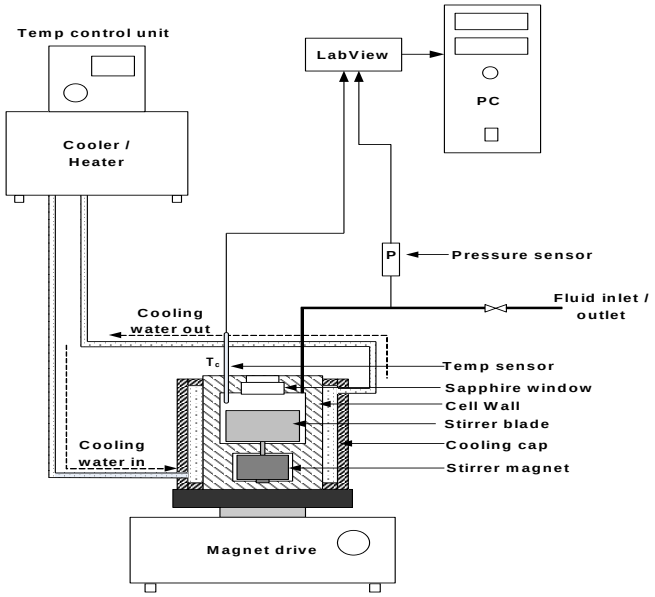

Figure1. Sketch of the experimental setup.

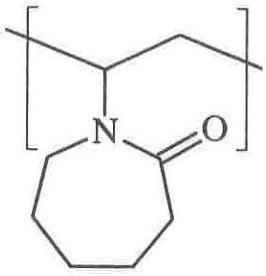

Figure 2. Monomer unit; Vinyl Caprolactam.

The experimental setup is shown in Figure 1 and incorporates a cell consisting of a titanium cylinder with top and bottom end piece. A stirrer blade is connected to a magnet house in the bottom end piece via an axle. An outer rotating magnetic field created by a laboratory stirrer bar drive was used to regulate the stirrer speed. The stirrer motor can be regulated to maintain speed in the range 0 to 1200 rpm. The free volume between the top and end pieces is 145 ml. The free volume (dead volume) around the stirrer magnet inside the magnet house is 8 ml. The cell is equipped with a cooling / heating jacket connected to a JULABO F34 HL refrigerated circulator, and temperature control is obtained by circulating water from the circulator. The desired temperature profile of the experiments is set on the temperature control unit and the temperature of the heating/cooling unit is regulated within a stability of ± 0.02 °C. The cell systems were equipped with 4-wire lead 1/10 DIN Pt-100 temperature sensors (accuracy ± 0.03 °C) and Rosemount 3051 TA absolute pressure transmitters. Pressure is measured in the inlet tubing and the temperature is measured inside the cell (in the vapour phase). The temperature was measured to an accuracy of ± 0.10 °C and pressure was believed measured to an accuracy of ± 0.5 bars.

Data were sampled on a computer using the LabView® data acquisition program. The experimental progress was continuously monitored on the computer screen during the experiments. At the end of the experiment data were transferred to office PC for analysis and graphical presentation.

Structure I, SII and SH hydrates were produced using three different hydrocarbon mixtures.

1. SI hydrates were formed from pure methane (Scientific grade 5.5, 99.9995 % purity),
2. SII hydrates were formed from a binary mixture of 92.5 % methane and 7.5 % propane
3. SH hydrates were formed from a mixture of pure methane and methylcyclohexane (C_7H_{14}).

The same procedure for preparation of the experiment and filling of the cell was followed in all experiments. A description of the general experimental procedure is described below.

1. The desired PVCap solution was prepared for the experiment.
2. The magnet house was filled with the aqueous solution and any air residue was squeezed out of the magnet section during mounting of the magnet house into the bottom end piece. Any residues of solution

on the top surface were removed prior to mounting the bottom end piece into the cell cylinder.

3. 50 ml of the aqueous solution was filled into the cell, and the top end piece was mounted.
4. The temperature of the heating/cooling unit was adjusted to 293 K prior to cell pressurization.
5. Prior to loading the cell to the experimental pressure it was purged twice with the natural gas mixture to be used by pressuring the cell to 60 bar. This was done to remove (dilute) any residues of air in the cell.
6. At 293 K the cell was loaded to the desired pressure while stirring, and the system was allowed to equilibrate before starting the experiment.
7. The stirring rate was kept constant at 750 rpm during the experiments.

Hydrates were formed at fixed temperature conditions by cooling the system down to the desired formation temperature. Hydrate formation was induced by magnetic stirring. The system was kept at the formation temperature for a period of time to produce the required amount of hydrates for the experiment. The hydrates were then dissociated by gradually increasing the cell temperature at preset heating rates. In a first stage the system was heated relatively fast to a temperature 4 – 5 degrees below the estimated equilibrium dissociation temperature applying a heating rate ($\delta T/\delta t$) of 1.0°K/h. At this point the heating rate was reduced to 0.2 °K/h or less, and the system was left at that rate until all hydrates were dissociated. In the vicinity of the final hydrate equilibrium point a low heating rate is required to provide uniform temperature equilibrium throughout the hydrate mass and the cell volume during the melting process. Heating rates as low as 0.0125 °K/h were applied in some of the experiments.

The pressure and temperature conditions in the cell were frequently sampled during the experiment. Hydrate formation was indicated by a sudden pressure drop in the cell due to gas leaving the vapour phase and entering empty cages in the hydrate structure. This can be seen in Figure 3, which describes a typical PT plot of sampled data during a run. The experiment is initiated at the right end of the baseline, from where the sample is cooled down. Hydrate formation is indicated by an increase in temperature and a decrease in pressure. This happens as gas molecules get enclathrated into the hydrate lattice and release of energy takes place. After the liquid has been transformed into hydrate, the temperature is increased applying the fast heating rate up to the point indicated by the first step on the dissociation curve. From this point and upward the heating rate was reduced to 0.2 °K/h or less. The final hydrate dissociation point is where the dissociation curve intersects the cooling curve (baseline). The region to the right of this point represents PT conditions for system without hydrates present. The hydrate dissociation point is the hydrate equilibrium point, where the initial conditions are resumed after a hydrate formation/decomposition cycle.

Measured hydrate dissociation temperatures were compared to hydrate equilibrium temperatures for corresponding non-inhibited systems using the CMSHYD prediction program from Sloan [12]. This is, to our knowledge, the only program available, which includes sH hydrate calculation. Discrepancies (ΔT) between experimental dissociation temperatures T(experimental) and predicted equilibrium temperatures T(CSMHYD) at the experimental pressure were calculated as:

$$\Delta T = T(\text{experimental}) - T(\text{CSMHYD})$$

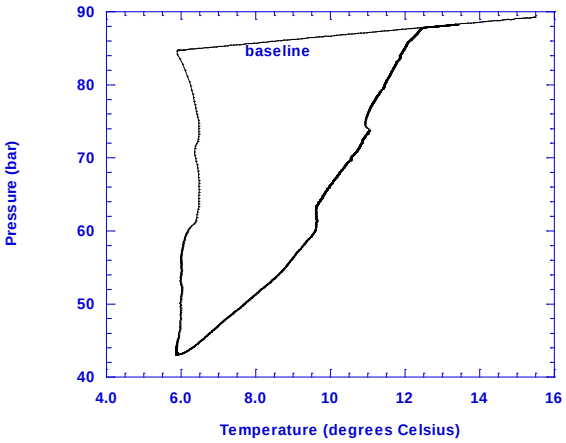

Figure 3. Pressure versus temperature plot obtained from experiment where hydrate formation is followed by hydrate dissociation.

RESULTS

For SI, SII and SH hydrates formed without PVCap, all measured hydrate dissociation temperatures were in good agreement with predicted (CSMHYD) values provided that the applied heating rate was equal to or less than 0.2 °C/h. Experimental dissociation temperatures for these systems were all within 0.15°C agreement with CSMHYD predicted values.

Measured dissociation temperature of sI (methane) hydrate formed in the presence of PVCap

Experiments were conducted by applying heating rates of; 0.2K/h, 0.025K/h and 0.0125K/h. Results are shown in Figure 4. The measured final hydrate dissociation temperatures were significantly displaced towards higher temperatures (i.e. ΔT>0) in all experiments. The displacement of the final hydrate dissociation temperature decreased towards a minimum (ΔT= 2.1 °K) when the heating rate was reduced to 0.0125 °K/h.

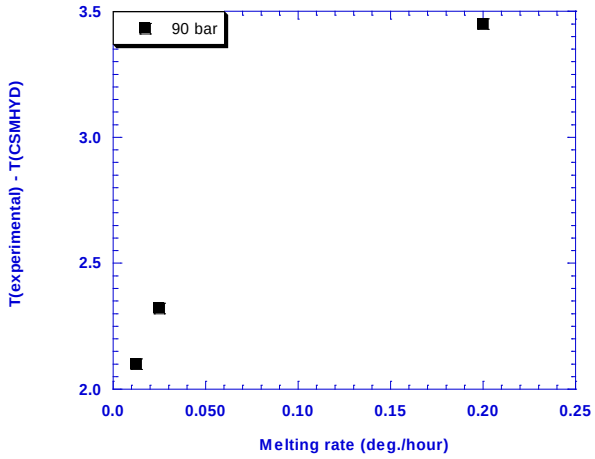

Figure 4. Temperature difference (ΔT) between measured dissociation value and calculated CSMHYD equilibrium temperature for different heating rates in a system containing CH_4 + 50ml of an aqueous solution containing 3000 ppm PVCap 2.5k.

Measured dissociation temperature of sII (methane-propane) hydrate formed in the presence of PVCap

Pressures in the region between 46 bar and 163 bar were applied. Dissociation temperatures corresponding to heating rates of 0.2K/h and 0.05K/h were determined. Temperature difference (ΔT) between the experimentally measured dissociation values and the corresponding calculated CSMHYD values are displayed in Figure 5.

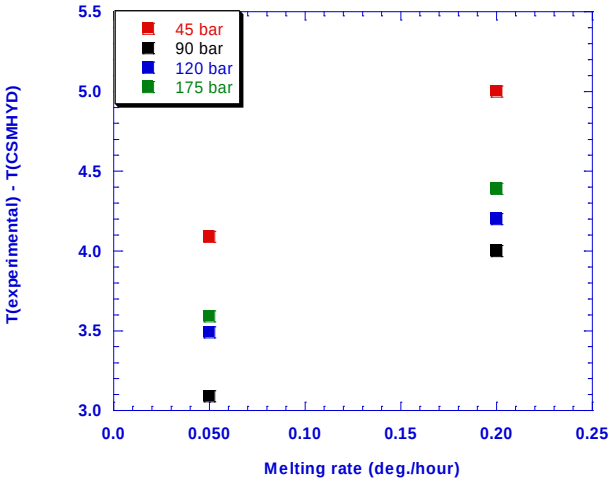

Figure 5. Temperature difference (ΔT) between the experimentally measured dissociation temperature and calculated CSMHYD equilibrium temperature for different heating rates in a system containing CH_4 + C_3H_8 + 50ml of an aqueous solution with 3000 ppm PVCap 6k.

Measured dissociation temperature of sH (methane-methylcyclohexane) formed in the presence of PVCap

Dissociation temperatures corresponding to melting rates of 0.2K/h and 0.05K/h were obtained. The temperature differences between the experimentally measured values and corresponding values given by CSMHYD are displayed in Figure 6.

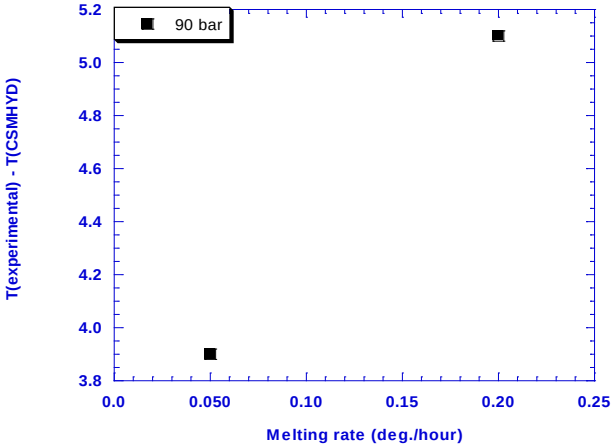

Figure 6. Temperature difference (ΔT) between measured dissociation value and calculated CSMHYD equilibrium temperature for different heating rates in a system containing CH_4 + C_7H_{14}

+ 50ml of an aqueous solution with 3000 ppm PVCap10k.

Data and results for the experiments in Figures 4-6 are summarized in Table 2.

Mw	Str.	Heating rate [deg/hour]	Pressure at 293 K [bar]	T(exp.)- T(CSMHYD)
2.5k	s I	0.2000	90	3,4
2.5k	s I	0.0250	90	2,3
2.5k	s I	0.0125	90	2,1
6.0k	s II	0.2000	46	5,9
6.0k	s II	0.0500	46	5,1
6.0k	s II	0.2000	115	5,2
6.0k	s II	0.0500	115	4
6.0k	s II	0.2000	163	5
6.0k	s II	0.0500	163	3,9
10.0k	sH	0.2000	90	5,1
10.0k	sH	0.0500	90	3,9

Table 2. Summary table for performed hydrate dissociation experiments

Discussion

Comparison of the inhibited systems with the non-inhibited systems for a given heating rate, revealed a significant increase in the temperature of dissociation for the inhibitor containing systems. Results indicate that the difference between the experimentally determined equilibrium point and the corresponding value calculated with CSMHYD, decreases with a decreasing heating rate. Dependence of the final dissociation value on the heating rate has also been documented by others [1,2]. Adsorption of kinetic inhibitors to the sII surface has been studied extensively by Carver et al. [3] and by Makogon [4] using Monte Carlo techniques. They found that kinetic inhibitors with lactam pendant groups adsorb to the hydrate surface with the lactam ring sterically stabilized in the 5^{12} 6^4 cavity. These results were also later confirmed by Freer and Sloan [5] making use of molecular dynamics simulations to predict the performance of kinetic inhibitor structures by simulating adsorption on the sII {111} hydrate growth plane. In the latter case, PVP (poly N-vinylpyrrolidone), PVCap (poly N-vinylcaprolactam) and PVVam (poly N-vinylvalerolactam) were compared. These kinetic inhibitors differ from each other only in the size of the lactam ring. The van der Waals forces as calculated from these simulations increased with increasing lactam ring size, a result which is consistent with the Lennard-Jones potential in that the potential energy increases due to attractive forces as the distance between the interacting molecules decreases. The distance between the carbon atoms that constitute the lactam ring and the water molecules representing the partially built cage will reduce as the ring size increases. More favorable interactions are obtained when this distance decreases, up to an optimal size. However, if the distance between the interacting molecules is smaller than the van der Waals bond length, then the interactions become repulsive. The van der Waals bond length corresponds to the distance between the interacting molecules where the potential is at a minimum. Consequently, the favorable interactions between the lactam ring and the large cavity (steric fit) are highly dependent on the size of the lactam ring. Dependence like this was observed by Freer and Sloan [5].

Habetinova et al. have found that hydrates formed in the presence of PVP have less influence on the dissociation than hydrates formed in the presence of PVCap [6].

The results presented in this paper reveal a clear kinetic influence of the inhibitor on the dissociation process. In addition to a clear kinetic effect there may also exist a thermodynamic effect. The existence of latter effect has also been suggested before [6]. A molecular dynamics study on the mechanism of kinetic inhibition by zwitterions was performed by Storr and Rodger [7]. They found that the presence of the zwitterions appeared to enhance the crystalline nature of the hydrate interface, which is consistent with the lock-and-key mechanism by which kinetic inhibitors are believed to work. The adsorption of a molecule tailored to the hydrate topology should in fact stabilize the hydrate structure. The presence of a kinetic inhibitor can lead to an increased order at the surface, and this leads to more efficient packing of the water. Reports regarding the hydrate morphology under the influence of kinetic inhibitors have revealed that the crystalline morphology of the hydrate is substantially altered by the addition of kinetic inhibitors [8, 9]. Lee and Englezos suggest that a proper term for the hydrate formed in the presence of kinetic inhibitors would be ‘hard’ versus soft

plugs formed in non-inhibited systems. It is plausible to believe that morphological alterations may influence the stability of the different cages that constitute the various hydrate structures.

CONCLUSION

Experiments were performed using sI, sII and sH hydrate formers with the kinetic inhibitor PVCap. Dissociation temperatures for each of the systems have been studied by applying different heating rates, as low as 0.0125 Kelvin per hour. Obtained results were consistent in the respect that the heating rate influenced the final temperature of hydrate dissociation. Heating rate is an experimental parameter that can lead to erroneous hydrate equilibrium predictions. However, even at very slow heating rates the inhibitor containing systems had significantly higher dissociation temperatures than the corresponding non-inhibited systems. The inhibitor shows a clear kinetic effect on the dissociation, but the results also indicate that there exists a thermodynamic effect. The hydrate structures apparently increased their stability under the influence of PVCap.

ACKNOWLEDGEMENTS

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