

INFLUENCE OF A SYNERGIST ON THE DISSOCIATION OF HYDRATES FORMED IN THE PRESENCE OF THE KINETIC INHIBITOR POLY VINYL CAPROLACTAM

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ABSTRACT

Laboratory tests have been performed using a stirred cell where SI and SII gas hydrates have been formed under the presence of the kinetic inhibitor Poly Vinyl Caprolactam (PVCap) and INHIBEX. The latter is a mixture containing 50wt% PVCap 2k and 50wt% butyl glycol. The effect of PVCap is enhanced by the presence of butyl glycol; the latter acts as a synergist for the former. Dissociation temperatures were obtained and compared for hydrates formed 1) in presence of PVCap and 2) in presence of INHIBEX. The effect of INHIBEX concentration on the temperature of dissociation was also investigated. Systems containing INHIBEX dissociated at lower temperatures than the corresponding systems with only PVCap present. Furthermore, 3000 ppm INHIBEX mixtures were found to have higher dissociation temperatures than 1500 ppm INHIBEX mixtures.

Keywords: gas hydrates, dissociation, kinetic inhibitors, synergist, INHIBEX, inhibitor dose

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

Natural gas hydrates can plug oil and gas production lines. Various chemical methods have been developed to prevent hydrate formation. Conventional methods involve injection of 20-50 wt% methanol in the water phase at the wellhead or downhole to depress the hydrate equilibrium temperature below the minimum fluid temperature in the line. However, high methanol injection rates may cause pipeline corrosion.

Certain water soluble polymers have been found to effectively inhibit hydrates [1]. The amounts needed are much lower than in the case of methanol, only 0.1-1.0 wt% of the water phase. The polymers slow down the rates of hydrate

nucleation and growth to such an extent that virtually no hydrates form in the wellstream during transport to processing facilities. The compounds are called kinetic inhibitors, and the most effective of them are vinylcaprolactam-based polymers. Examples of this type that are widely used are poly-vinylcaprolactam (PVCap), poly-vinylpyrrolidone (PVP) and a terpolymer of vinylcaprolactam, vinylpyrrolidone and (dimethylamino)ethyl meth-acrylate named Gaffix VC-713. Small amounts of glycol ethers (ex. 2-butoxyethanol) have been found to substantially improve the performance of the polymeric hydrate inhibitors [1]. A combination of VC-713 and less than 1 wt% of certain glycol ethers were found to have a synergic effect on retarding hydrate methane formation [2]. A mixture of VC-713 (0.5 wt% of water phase) and ethylene glycol butyl ether (0.75 wt% of water phase) resulted in an increased induction time by a factor of 30 (from 40 minutes to 1200 minutes). The induction time without additives was 0 min. [2].

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EXPERIMENTAL PROCEDURE AND DESCRIPTION

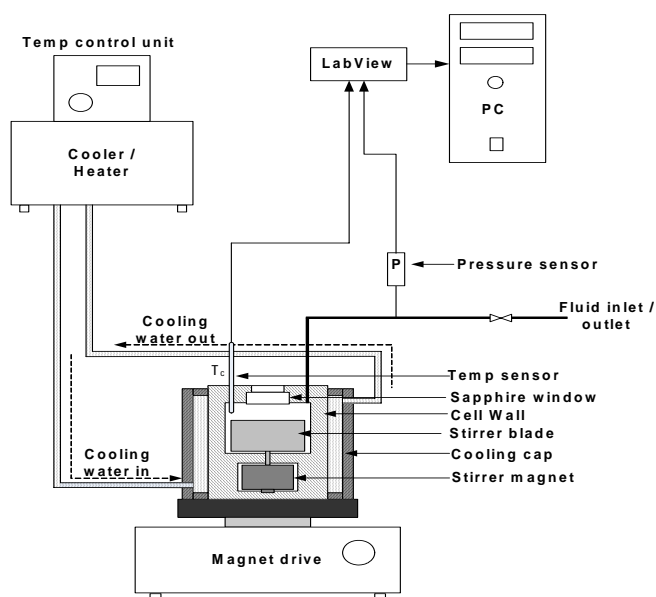


Figure1. Experimental setup applied in gas hydrate experiments.

Gas hydrates were formed from solutions containing either the kinetic inhibitor Poly Vinyl Caprolactam ($M_w=2.5k$) or INHIBEX. The latter is a liquid mixture containing 50wt% PVCap 2k and 50wt% butyl glycol. The effect of PVCap is enhanced by the presence of butyl glycol; the latter acts as a synergist for the former.

All tests were performed using the experimental setup shown in Figure 1. 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.

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

1. INHIBEX solutions and PVCap solutions were prepared.
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.

The temperature profile of the heating/cooling unit was set on the temperature controller. 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 using 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 and kept until all hydrates were dissociated. Obtained dissociation temperatures were compared for hydrates formed 1) in the presence of PVCap and 2) in presence of INHIBEX. The effect of INHIBEX concentration on the temperature of dissociation was also investigated.

RESULTS

50 ml solution containing 1500 ppm INHIBEX was loaded into a cell. Another cell was loaded with the same amount of inhibitor, without butyl glycol present in the mixture. For the experiments

both cells were pressurized with methane, and different pressures were applied (45bar at 20°C and 90 bar at 20°C). Temperatures of dissociation were obtained for the different systems; (1) PVCap + butyl glycol and (2) pure PVCap. Results are displayed in Figure 2.

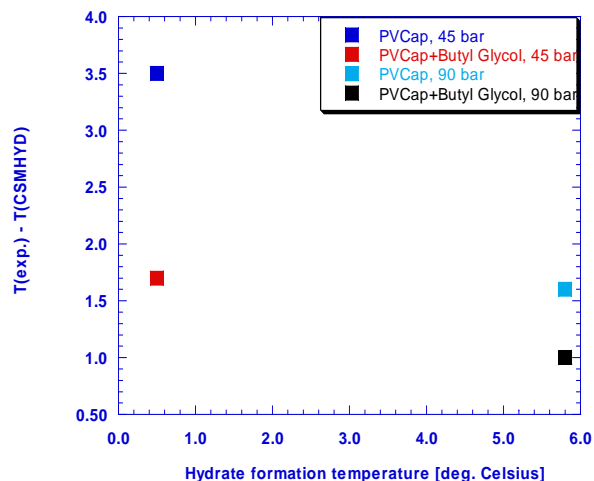


Figure 2. Difference between experimental dissociation temperature and corresponding value calculated by CSMHYD for SI hydrate formed under the influence of PVCap versus INHIBEX.

50 ml solution containing 3000 ppm INHIBEX was loaded into a cell, while another cell was loaded with the same amount of solution only containing PVCap. Some experiments were performed by pressurizing the cells with methane and other experiments used a methane-propane mixture. Different pressures were applied; 30 bar, 60 bar, 90 bar and 120 bar at 20°C. The influence of the (PVCap + butyl glycol)-system versus the PVCap-system on the temperature of dissociation was investigated. Results for pure methane are displayed in Figure 3, and results for the methane propane mixture are shown in Figure 4.

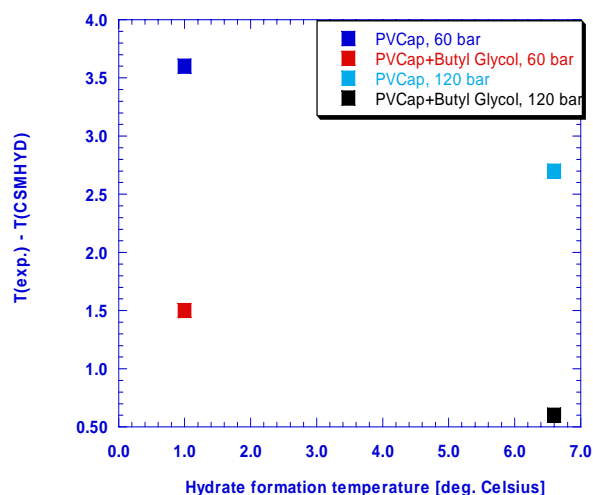


Figure 3. Difference between experimental dissociation temperature and corresponding value calculated by CSMHYD for SI hydrate formed under the influence of PVCap versus INHIBEX.

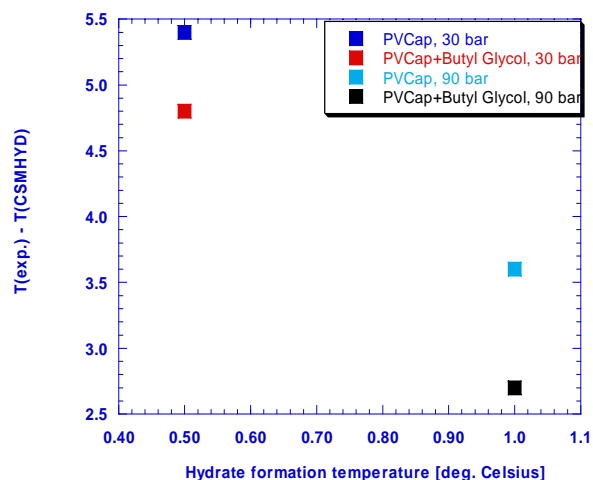


Figure 4. Difference between experimental dissociation temperature and corresponding value calculated by CSMHYD for SII hydrate formed under the influence of PVCap versus INHIBEX.

To study the effect of INHIBEX concentration on the temperature of dissociation, doses of 1500 ppm and 3000 ppm were used. 50 ml solution containing 1500 ppm INHIBEX was loaded in a cell. Another cell was loaded with 50 ml of the solution containing 3000 ppm INHIBEX. Both cells were pressurized with pure methane to 60 bar at 20°C (Figure 5), 95 bar at 20°C (Figure 6) and 120 bar at 20°C (Figure 7). Differences between measured dissociation temperatures and calculated values are shown in Figures 5-7.

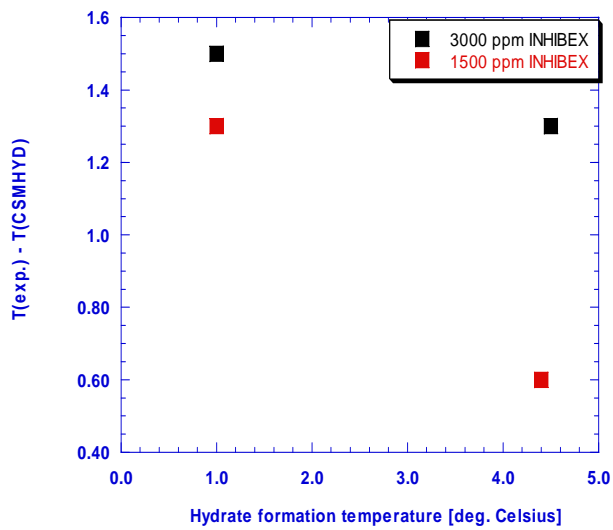


Figure 5. Difference between experimental dissociation temperature and corresponding value calculated by CSMHYD for different formation temperatures for SI hydrate formed with INHIBEX.

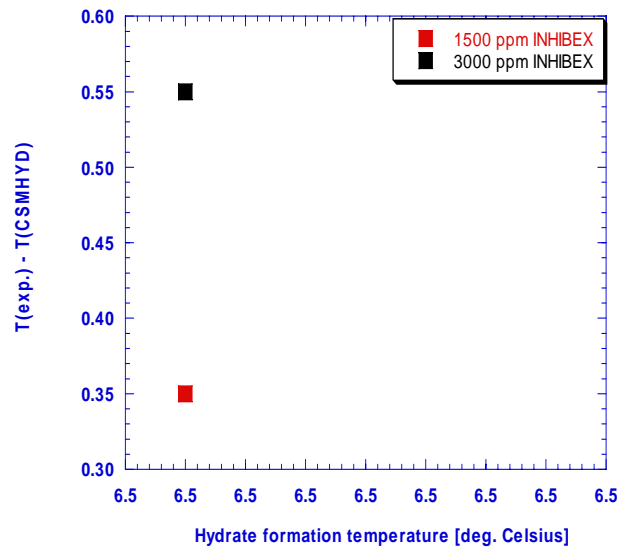


Figure 7. Difference between experimental dissociation temperature and corresponding value calculated by CSMHYD for SI hydrate formed with INHIBEX.

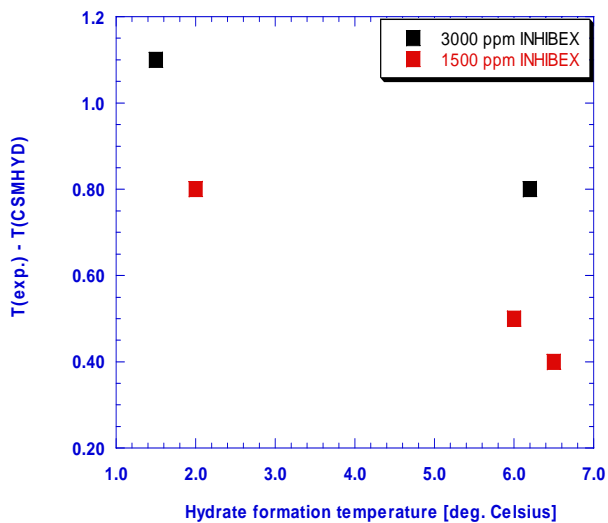


Figure 6. Difference between experimental dissociation temperature and corresponding value calculated by CSMHYD for various formation temperatures for SI hydrate formed with INHIBEX.

Str.	PVCap2k (ppm)	Butyl Glycol (ppm)	P (bar)	T ₀ (°C)	T _(exp.) - T _(CSMHYD)
sl	750	750	45	0.5	1.7
sl	750		45	0.5	3.5
sl	750	750	90	5.8	1
sl	750		90	5.8	1.6
sl	1500	1500	60	1	1.5
sl	1500		60	1	3.6
sl	1500	1500	120	6.6	0.6
sl	1500		120	6.6	2.7
sll	1500	1500	30	0.5	4.8
sll	1500		30	0.5	5.4
sll	1500	1500	90	1	2.7
sll	1500		90	1	3.6

Table1. Summarized results for Figures 2-4.

PVCap2k (ppm)	Butyl Glycol (ppm)	P (bar)	T ₀ (°C)	T _{exp.} - T _{CSMHYD}
750	750	60	1	1.3
750	750	60	4.5	0.6
1500	1500	60	1	1.5
1500	1500	60	4.5	1.3
750	750	95	2	0.8
750	750	95	6	0.5
750	750	95	6.5	0.4
750	750	120	6.6	0.4
1500	1500	95	1.5	1.1
1500	1500	95	6.2	0.8

Table2. Summarized results for Figures 5-7 (sl hydrates only).

DISCUSSION

Both sI and sII systems exhibit significant discrepancies between the measured dissociation temperatures for the INHIBEX systems versus the corresponding PVCap systems. Solutions containing both butyl glycol and PVCap exhibit lower dissociation temperatures than solutions containing only PVCap. Gas hydrates formed in the presence of PVCap apparently gain increased stability [4]. Obtained experimental results indicate that the presence of butyl glycol in addition to PVCap decreases the hydrate dissociation temperature observed for PVCap systems.

Hydrate SI systems exhibit similar trends regarding the discrepancy in T_{diss} for the systems at pressures of 60 bar, 95 bar and 120 bar containing different doses of INHIBEX. All systems exhibit a higher dissociation temperature for the solutions containing 3000 ppm INHIBEX compared to 1500 ppm. Results furthermore revealed that pressure is a parameter influencing the magnitude of the discrepancy in T_{diss} (ΔT_{diss}). For pressures around 60 bar ΔT_{diss} increased with increasing formation temperature (T_0). At $T_0 = 1^\circ\text{C}$ and $T_0 = 4.5^\circ\text{C}$ obtained values for ΔT_{diss} were 0.2°C and 0.7°C , respectively. Increasing the pressure to 95 bar gives identical values for ΔT_{diss} , irrespective of whether the hydrate formation takes place at 2°C or 6°C . Hydrate formation at 6.5°C at approx. 95 bar and 120 bar resulted in comparable deviations (ΔT) from the values predicted by CSMHYD. Higher pressure (120 bar) gave somewhat reduced ΔT when compared to lower pressure (95 bar).

Cohen et al. have performed experiments where the influence of the concentration of 2-butoxyethanol on the induction time was investigated. The 2-butoxyethanol concentration was varied while holding a constant 0.5 wt% VC-713 concentration. Results revealed a peak in the induction time around 0.5-0.75 wt% 2-butoxyethanol. At higher concentrations the induction time decreased strongly, even though the results were better than for systems with VC-713 without glycol ether present [2].

Glycol ethers are known to have surfactant-like properties [3]. An explanation of the improved performance of kinetic inhibitors in the presence of glycol ethers has already been proposed [2]. The hydrophobicity of the alkoxy group may cause the molecules to associate with the dissolved polymer. This could alter the conformation of the

polymer in solution. An extended polymer would presumably have more of its length available for interaction with the hydrate crystal.

CONCLUSION

Higher Inhibex doses (3000 ppm) resulted in an elevated temperature of dissociation compared to the solutions containing 1500 ppm INHIBEX. At pressures of approx. 60 bar the discrepancy in the temperature of hydrate dissociation between the different doses increased with the formation temperature. Higher pressures seemed to somewhat reduce the discrepancy between experimentally measured dissociation temperatures and CSMHYD predicted values.

ACKNOWLEDGEMENTS

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