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Powerful Synergy of Acetylenic Diol Surfactants with Kinetic Hydrate Inhibitor Polymers—Choosing the Correct Synergist Aqueous Solubility

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Cite This: *Energy Fuels* 2021, 35, 15721−15727

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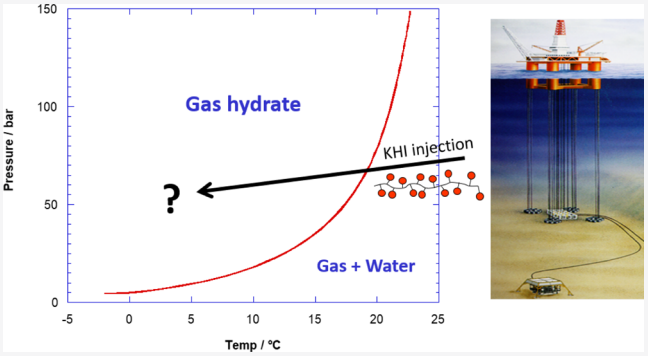
ABSTRACT: The performance of injected kinetic hydrate inhibitor (KHI) polymer solutions can be boosted considerably by judicious choice of the polymer solvent system. We report the excellent KHI synergism of the low-foaming acetylenic diol gemini surfactant 2,4,7,9-tetramethyl-5-decyne-4,7-diol (TMDD) with poly(*N*-vinyl caprolactam), *N*-vinyl caprolactam:*N*-vinyl pyrrolidone copolymer, and poly(*N*-isopropylmethacrylamide). High-pressure rocking cell tests, using the slow constant cooling method or the isothermal method, were carried out with a natural gas mixture giving structure II hydrates as the preferred thermodynamically stable phase. Poly(oxyethylene) derivatives of TMDD, which are far more water-soluble than TMDD, gave significantly lower synergetic KHI performance with the same polymers. It is conjectured that the low aqueous solubility of TMDD (1700 ppm at 20 °C) and its two isobutyl groups are key features contributing to the synergism. However, when decane was added to the system as a model liquid hydrocarbon phase, the synergetic performance decreases, probably due to partitioning of TMDD to the hydrocarbon phase. This highlights the need to choose synergist systems which are retained in the aqueous phase for optimal performance when condensate or oil is present in the produced fluids. Optimizing the structure and aqueous solubility of the synergist (solvent or otherwise) can be seen as complementary to the known principle of optimizing the structure and solubility of the KHI polymer.



1. INTRODUCTION

Gas hydrates are ice-like solids that are formed under conditions of elevated pressure and low temperatures, which are common conditions in gas and oil transportation flow lines.[1−3] These flow lines may be subsea or on land in cold-climate regions. Gas hydrate blockages in flow lines are a major challenge for flow assurance in the upstream gas and oil industry.[4−10] The most common chemical method to prevent gas hydrate blockages is the use of thermodynamic inhibitors (antifreezes), such as methanol, monoethylene glycol, and electrolytes.[11,12] However, high concentrations (often 20−60 wt % of the water present) are required, necessitating high capital and operational costs.[13]

An alternative method that has been in use since the mid-1990s is deployment of kinetic hydrate inhibitors (KHIs).[13−17] The main component of a liquid and pumpable KHI formulation is one or more water-soluble polymers in one or more solvents. The solvent and various classes of non-polymeric synergists can be added to improve the performance. Typical effective polymers include poly(*N*-vinyl caprolactam) (PVCap) and poly(*N*-*iso*-propyl methacrylamide) (PNIPMAM) and copolymers thereof (Figure 1). Both PVCap and PNIPMAM have quite low cloud points in water at typical KHI polymer dosages of 0.1−1.0 wt % based on the water phase. We proposed that a low polymer cloud point (i.e., near-hydrate-forming temperatures) is a useful property for high KHI performance as long as certain other criteria are met.[18] These included sufficient pendant amphiphilic groups with good hydrogen-bonding (e.g., amide or amine oxide) and correct-size hydrophobic groups. Placing these groups in a low-molecular-weight polymer or oligomer can be beneficial for KHI performance because it gives a high polymer surface area/hydrodynamic volume (or surface area/weight) ratio and often a lower cloud point than higher-molecular-weight polymers.

Following on from this study, we determined that alcohols and glycols, which also were close to their solubility limit at

Received: August 6, 2021
Revised: September 8, 2021
Published: September 19, 2021

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https://doi.org/10.1021/acs.energyfuels.1c02152
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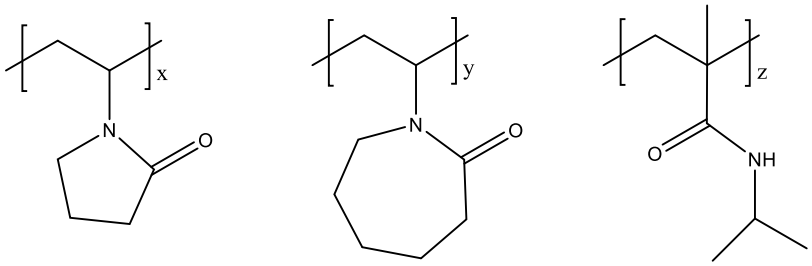

Figure 1. Structures of typical KHIs. From right to left: PVP, PVCap, and PNIPMAM.

typical KHI dosages and had the correct-size hydrophobic groups, performed well as KHI synergists for PVCap.[19] In particular, 4-methylpentan-1-ol (iHexOl) showed remarkable synergy, greater than classic KHI solvents such as butyl glycol ether (BGE). 4-Methyl-1-pentanol has a flash point of 57 °C and a water solubility of 7.6 g/L (i.e., 7600 ppm) at 20 °C, which is in the range of the KHI polymer solvent at typical field dosages. Another alcohol with a similar solubility is cycloheptanol. This also showed better synergy with PVCap than smaller cycloalkanols.

Recently, another class of synergists, those of ethoxylated acetylenic diols, was shown to give good synergy with a 1:1 commercial VP/VCap copolymer.[20] These synergists are nonionic surfactants, also sold under the trade names Surfynol 465 and Surfynol 485, with the chemical names being 2,4,7,9-tetramethyl-5-decyne-4,7-diol decaethoxylate (TMDD-EO10) and TMDD tricontaethoxylate (TMDD-EO30). In high-pressure tests using methane gas, a 1:2 mixture of VP/VCap copolymer and TMDD-EO10 gave the best performance. TMDD-EO10 is characterized by high solubility in water, low foaming, and lower cost than the vinyl lactam-based KHI.

Based on our earlier work regarding the powerful synergy of the sparingly soluble iHexOl with PVCap, it occurred to us that it might be possible to increase the synergy of TMDD-EO10 by reducing or even removing the ethoxylate groups to give a surfactant that is more sparingly soluble in water, just a few thousand ppm. The unethoxylated surfactant is TMDD. It is used on a large scale as a wetting and antifoaming agent in the paper, ink, pesticide, and adhesive industries.[21] The physicochemical properties indicate only slow biodegradation, but due to its HLB of about 8, it has low bioaccumulation potential.

The solubility of TMDD in water is about 0.2 g/L (2000 ppm) at 20 °C which we thought was about the right level for a sparingly soluble KHI polymer synergist.[22] TMDD is made by the reaction of methyl isobutyl ketone with a base and two equivalents of sodium carbide or ethyne.[23] In the process of making TMDD, the intermediate 5-methyl-1-hexyn-3-ol (5-MH) is formed. This is also commercially available. TMDD is a gemini surfactant with two isobutyl groups, whereas 5-MH has only one. This study investigates the synergistic properties of 5-MH, TMDD, and TMDD-EO10 with PVCap and PNIPMAM in high-pressure slow constant cooling (SCC) experiments with a synthetic natural gas mixture. Experiments to study the effect of the addition of a liquid hydrocarbon to the KHI test solution were also carried out.

2. EXPERIMENTAL SECTION

2.1. Materials. 1-Bromo-2-methyl-propane, tetrahydrofuran, TMDD (mixture of ± and meso), TMDD decaethoxylate, and 5-methyl-1-hexyne-3-ol were purchased from VWR (Avantor). PVCap (M_w = 8−10 kg/mol) was supplied from BASF as a 41.1 wt % ethylene glycol solution but with the solvent being removed. A lower-molecular-weight PVCap (Inhibex 101, abbreviated here as PVCap/BGE) was supplied by Ashland chemical company as a 50 wt % solution in BGE.

2.2. KHI Performance Tests. Similar to many of our previous studies, the KHI performance tests were carried out in a high-pressure rock rig with five cells (RC5), supplied by PSL Systemtechnik, Germany.[24−26] Each cell contains a stainless-steel ball (ca. 15 mm diameter) for agitation of the fluids. A synthetic natural gas (SNG) mixture (Table 1) was used to provide the high-pressure gas hydrate formation atmosphere. The SNG was prepared by Praxair, Norway, and the composition was analyzed before sale to be within ±0.1% of all the required concentrations. For the sensors, the maximum pressure error is ±0.2 bar and the maximum temperature error is ±0.1 °C, as previously reported.[27] Pressure and temperature sensors are calibrated using the "calibration dialogue" box in the rocking cell software.

Table 1. Composition of the SNG Mixture

component	mol %
nitrogen	0.11
n-butane	0.72
isobutane	1.65
propane	5.00
CO_2	1.82
Ethane	10.3
methane	80.4

2.3. SCC Tests. These were carried out to evaluate the KHI performance of the polymers and synergists. The procedure for SCC tests was as follows:

1. Around 105 mL of KHI solution with dissolved maleamide polymers in it was prepared at least 1 day before the KHI performance tests to ensure complete dissolution. Around 20 mL of the KHI solution was added to each cell.
2. The procedure of purging with SNG and then vacuum was applied twice to remove the air in the system.
3. Approximately 76 bars of SNG was loaded to each cell at a temperature of 20.5 °C. The gas inlet/outlet valve of each cell was then turned off, so each cell was a separately closed system. The equilibrium temperature (T_{eq}) for sII gas hydrate at 76 bar was predicted to be 20.5 °C using the PVTSim software, Calsep.[28]
4. The cells were slowly cooled down at a cooling rate of 1 °C/h and rocked at a rocking rate of 20 full swings/min with maximum 40°. The pressure and temperature data during the cooling period were recorded using sensors.

An example of the pressure−time and temperature−time curves obtained from one experiment is shown in Figure 3.

The determination of hydrate onset temperature (T_o) and rapid hydrate formation temperature (T_a) from the temperature and pressure curves obtained from one cell can be seen in Figure 4. In the closed system, the pressure decreased linearly due to the constant

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Energy Fuels 2021, 35, 15721−15727

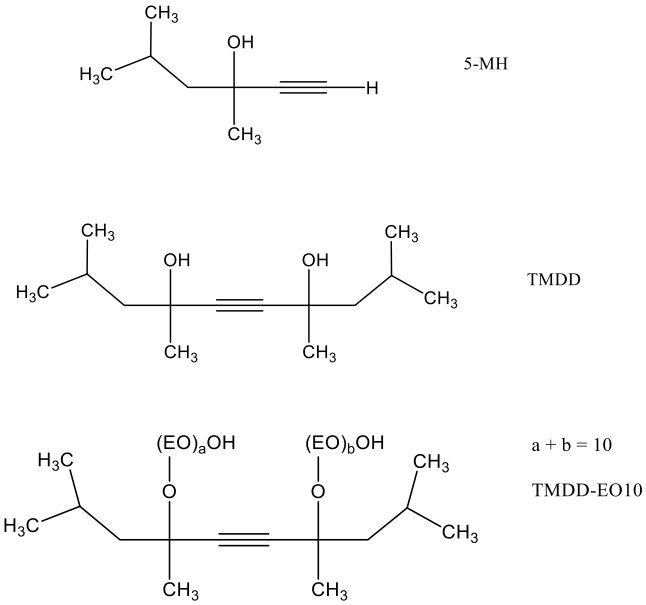

Figure 2. 5-Methyl-1-hexyn-3-ol (5-MH); TMDD; and TMDD decaethoxylate (TMDD-EO10).

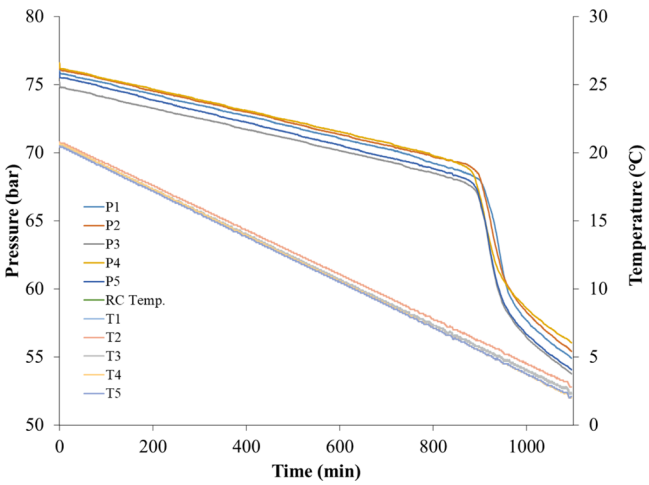

Figure 3. Example of a set of SCC pressure−time and temperature−time graphs obtained from all five cells. (RC temp. is the cooling bath temperature).

cooling of the temperature. Once gas hydrates started to form, the pressure deviated from the original linear track, and this first pressure drop point was marked as P_o. The corresponding temperature at P_o was determined as T_o. The fastest pressure drop point was marked as P_a and its corresponding temperature was determined as T_a.

2.4. Isothermal Test Procedure.[29] The flushing of the rocking cells was carried out as the same as for the SCC tests. Then, the cells were charged with 75 bar SNG at 20.5 °C. The fluids were cooled with rocking (the same rate as for SCC tests) to the experimental temperature (6.0 or 4.0 °C) and held at this temperature for at least 48 h. When the cells are cooled to 4 °C, the pressure drops to ca. 68 bar. The equilibrium temperature (T_{eq}) is ca. 19.8 °C at this pressure predicted using PVTSim software. This means that the subcooling (ΔT) is ca. 15.8 °C. The starting time at the set temperature is taken as time zero. From the pressure drop or gas consumption curves, as shown in Figure 5, it is possible to determine the hold time, t_i, as the start of detectable hydrate formation, and the fast hydrate growth time, t_a, as the time when the growth rate is first at its fastest. It should be noted that nucleation may have started before the hold time.

3. RESULTS AND DISCUSSION

The results obtained from SCC tests are summarized in Table 2. Deionized water (DIW) and PVCap (M_w = 8−10 kg/mol) by itself were also tested for comparison. Results of synergetic tests with mono-*n*-BGE, butyl diglycol ether (BDGE), and 4-methyl-1-pentanol (iHexOl) are included from previous studies carried out by the same person, under identical test conditions and in the same equipment.[19]

We begin a discussion of the results by looking at the motivation for this study, that is, whether TMDD is a better synergist for KHI polymers than the more water-soluble TMDD-EO10. The SCC test results in Table 3 clearly show that TMDD or TMDD-EO10 used alone is very poor KHIs with average T_o values only a little better than water. For PVCap, the synergy of TMDD-EO10 is a little weaker than that for BGE. TMDD-EO10 shows negligible synergy with the VP/VCap copolymer and only weak synergy with PNIPMAM. However, when used in combination with all three polymers, TMDD (5000 ppm) is a far better synergist than TMDD-EO10. The synergy of TMDD appears to be the most powerful (greatest drop in onset temperature) for PVCap with the average T_o dropping from 10.4 °C for PVCap alone to no hydrates at a minimum test temperature of 2 °C. Using a lower concentration of TMDD (2500 pm) gives a smaller decrease in the onset temperature, now with a measurable average T_o value of 4.3 °C. The only alcohol previously found to have comparable synergy in blends with PVCap is iHexOl, which also gave no hydrates down to the minimum test temperature, in this case, 3 °C.

TMDD and the ethoxylated derivatives are unusual small di amphiphiles that have a triple bond in the middle. We speculate that the strong synergy of TMDD is related to several factors, including solubility, dual hydrophobic head groups, and the optimum shape and size of these isobutyl groups. These factors are discussed below. The alkyne triple bond may also be important for the KHI synergy by having no rotation and fixing the two isobutyl end groups to be kept away from each other. We would have liked to investigate the hydrogenated version of TMDD, which would have a C−C single bond in the middle that does rotate, but this was not commercially available.

TMDD at 5000 ppm gives a cloudy solution either alone or when mixed with 2500 ppm of the polymers. According to various nonpeer-reviewed online sources, the solubility of TMDD (or Surfynol 104 as one of its trade names) at 20 °C is 1.7 g/L (1700 ppm). We checked the limit of solubility in our hands and we found that solutions up to 900 ppm gave clear solutions but 1000 ppm and higher concentrations gave some insoluble materials as small flakes. This may change during SCC tests as the temperature decreases to 2 °C. The solubility of TMDD is thus fairly low. In comparison, the synergist solvent iHexOl has a solubility of 7.6 g/L in water (7600 ppm) at 20 °C, somewhat higher than that of TMDD.[19] As discussed previously, it seems that alcohols or glycols, with the correct-size and -shape hydrophobic alkyl groups, when applied close to their solubility limits are good synergists particularly for PVCap (We will be exploring the synergy of iHexOl with polymers other than PVCap in a subsequent publication). When close to the solubility limit, a solvent will give maximum hydrophobic interactions with bulk water or growing hydrate particles. This solubility factor is akin to the improved performance of KHI polymers when they have low cloud

https://doi.org/10.1021/acs.energyfuels.1c02152
Energy Fuels 2021, 35, 15721−15727

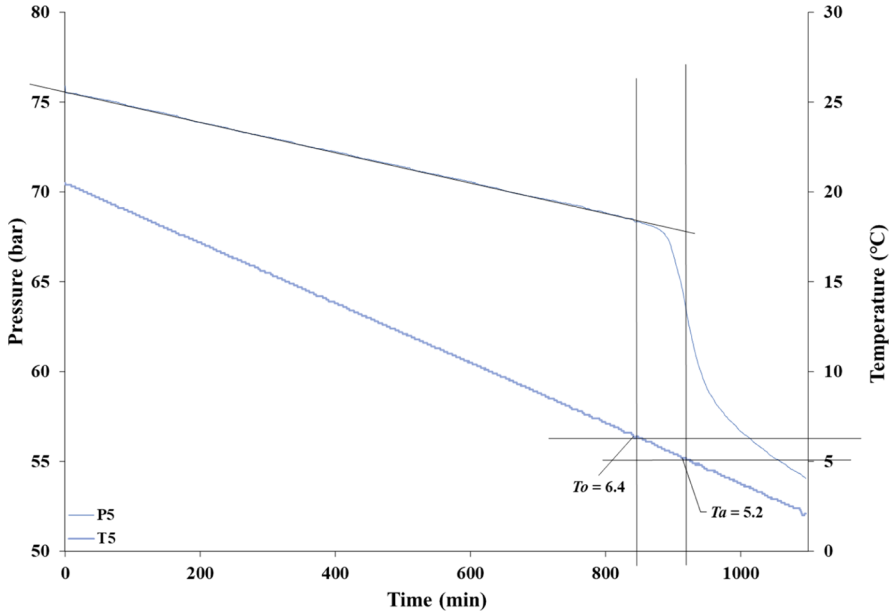

Figure 4. Determination of T_o and T_a values for one rocking cell.

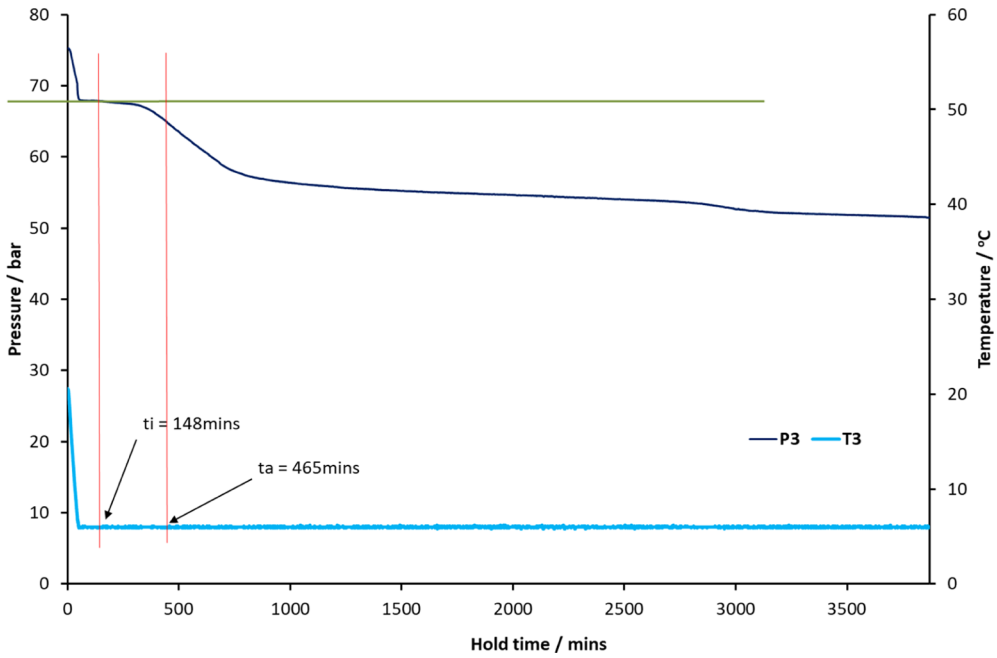

Figure 5. Determination of hold time (t_i) and fast growth time (t_a) in an isothermal test in cell 3 at 6.0 °C and 68 bar (ΔT ca. 13.8 °C).

points (less than about 40 °C), for example, PVCap or PNIPMAM.[18]

TMDD can be thought of as having two terminal isobutyl groups (Figure 2). The usefulness of isobutyl groups in solvent synergists has also been seen previously. We suggested that tail-branched alkyl groups, such as isobutyl, give better synergy with PVCap than the straight chain. See, for example, results in Table 3 for the glycols BGE and isobutyl glycol ether (iBGE) in combination with PVCap or PNIPMAM.[30]

The final factor we considered as important for the powerful synergy of TMDD is that it contains two hydrophobic groups. To determine the significance of the twin hydrophobic end groups, we also investigated 5-MH, which is as close to half the molecule as is commercially available, with only one isobutyl end group. The addition of 5000 ppm 5-MH to PVCap gave good synergy, on a par with iBGE or BDGE, but clearly not as good as either TMDD or iHexOl. There are probably two reasons for this observation. Solutions of 5000 ppm 5-MH alone or with 2500 ppm polymer are clear at 20 °C indicating that 5-MH is more soluble in water than TMDD or iHexOl. As discussed earlier, sparingly soluble solvents, with the correct-size and -shape hydrophobic groups, appear to give better synergy than more soluble solvents as this maximizes the hydrophobic interactions with water or hydrate particles.

3.1. Effect of the Gas–Water Ratio and Liquid Hydrocarbon Phase. Gas fields with associated produced water are currently the main application for KHIs. Gas fields usually have some liquid hydrocarbon production. Therefore, as we knew that TMDD was sparingly soluble in water, we wanted to investigate the effect of adding some liquid

https://doi.org/10.1021/acs.energyfuels.1c02152
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Table 2. Summary Information of KHI SCC Tests[a]

polymer	synergist	[synergist] ppm	T_o (av.) ± deviation [°C]	T_a (av.) ± deviation [°C]	T_o (av.) − T_a (av.) [°C]
DIW			17.2 ± 0.6	16.7 ± 0.5	0.5
	5-MH	5000	16.7 ± 0.4	16.1 ± 0.5	0.6
	TMDD[d]	5000	15.6 ± 0.4	15.2 ± 0.4	0.4
	TMDD-EO10	5000	15.7 ± 0.3	15.5 ± 0.3	0.2
PVCap			10.2 ± 0.3	8.8 ± 0.5	1.4
PVCap	-[b]		10.6 ± 0.5	9.3 ± 0.1	1.3
PVCap	-[c]		9.5 ± 0.2	8.8 ± 0.2	0.7
PVCap	BGE	5000	7.3 ± 0.4	3.8 ± 0.4	3.5
PVCap	BDGE	5000	5.5 ± 0.4	2.9 ± 0.4	2.6
PVCap	iBGE	5000	5.7 ± 0.4	2.5 ± 0.3	3.2
PVCap	iHexOl	5000	<3.0	<3.0	
PVCap	5-MH	5000	5.4 ± 0.4	3.9 ± 0.3	1.5
PVCap	TMDD[d]	2500	4.3 ± 0.5	3.0 ± 0.3	1.3
PVCap	TMDD[d]	5000	<2.0	<2.0	
PVCap	TMDD[bd]	5000	2.8 ± 0.2	2.2 ± 0.2	0.6
PVCap	TMDD[d]	5000	5.9 ± 0.5	4.8 ± 0.5	1.1
PVCap	TMDD-EO10	2500	8.8 ± 0.3	7.8 ± 0.2	1.0
PVCap	TMDD-EO10	5000	8.3 ± 0.4	8.0 ± 0.3	0.3
VP/VCap			8.1 ± 0.9	5.7 ± 0.4	2.4
VP/VCap	BDGE	5000	6.8 ± 0.4	4.2 ± 0.3	2.6
VP/VCap	5-MH	5000	7.0 ± 0.6	4.5 ± 0.4	2.5
VP/VCap	TMDD[d]	5000	5.5 ± 0.4	3.7 ± 0.3	1.8
VP/VCap	TMDD-EO10	5000	8.2 ± 0.6	5.9 ± 0.2	2.3
PNIPMAM			10.5 ± 0.8	10.2 ± 0.6	0.3
PNIPMAM	BGE	5000	6.2 ± 0.8	5.0 ± 0.3	1.2
PNIPMAM	iBGE	5000	5.5 ± 0.5	4.2 ± 0.2	1.3
PNIPMAM	iHexOl	5000	4.6 ± 0.8	2.9 ± 0.3	1.7
PNIPMAM	5-MH	5000	7.2 ± 0.2	5.5 ± 0.2	1.7
PNIPMAM	TMDD[d]	5000	5.8 ± 0.4	3.2 ± 0.4	2.6
PNIPMAM	TMDD-EO10	5000	8.8 ± 0.4	8.2 ± 0.2	0.6

[a]Average of five tests using 20 mL of aqueous solution unless otherwise stated. [b]15 mL. [c]15 mL + 1 mL decane. [d]Cloudy solution.

Table 3. Isothermal Test Results Using 2500 ppm PVCap and Synergist

polymer	concn. Ppm	synergist	concn. ppm	temp. °C	ΔT °C	hold time (t_o) min	fast growth time (t_a) min
PVCap	2500			6	13.8	80−90[a]	80−100[a]
PVCap	2500	iBGE	5000	6	13.8	117, 119, 148, 128, 123 (Av. 127)	421, 398, 465, 476, 487
PVCap	2500	TMDD	5000	4	15.8	523, 826, 716, 679, 572 (Av. 663)	763, 1180, 1063, 968, 899 (Av. 974)
PVCap	2500	TMDD[b]	5000	4	15.5[c]	95−100[d]	95−100
PVCap	7500			4	15.8[e]	100−150	100−155
PVCap	7500	TMDD	5000	4	15.8[e]	624, 366, 348, 371, 286 (Av. 398)	<1 bar pressure drop due to hydrates in 3600 min
PVCap	7500	TMDD	5000	4	15.5[bce]	324, 279, 282, 263, 272 (Av. 284)	<1 bar pressure drop in 3600 min

[a]Hydrates formed before reaching 4 °C. [b]1 mL of decane was also added. [c]Calculated.[28] [d]Hydrate formation started in all cells on reaching approximately 4 °C. [e]15 mL of aqueous solution.

hydrocarbon to the test cells as some of the TMDD might partition to this phase lowering its activity in the aqueous phase. We also lowered the total liquid volume to 16 mL, made up of 15 mL of aqueous phase and 1 mL of decane as a model hydrocarbon phase.

Reducing the liquid volume to 16 mL made sure the steel balls are not fully covered in liquid, which could affect the efficacy in rocking cell tests. An earlier study with *N*-vinyl lactam-based polymers has shown that reducing the volume of the aqueous KHI solution from 20 to both 15 to 10 mL gave a small but significant reduction in the performance (SCC or isothermal tests).[31]

Reduction of the aqueous PVCap solution (2500 ppm) from 20 to 15 mL gave slightly higher average T_o (10.2 °C for 15 mL instead of 10.6 °C) and T_a values but statistically insignificant at the 95% level given the variation in test results. However, 15 mL of a solution containing 2500 ppm PVCap and 5000 ppm TMDD gave a significantly higher T_o value of 2.8 °C compared to using 20 mL of solution which gave no macroscopic hydrates down to a minimum temperature of 2 °C. Furthermore, when 1 mL of decane as a model liquid hydrocarbon was added to 15 mL of the same synergistic mixture, the average T_o value increased to 5.9 °C. We believe that the poorer KHI performance is related to the partitioning of the sparingly water-soluble TMDD to the decane phase. We have attempted to determine the partitioning percentage in using the mixture of water and decane and TMDD shaken in a separation funnel, but the formation of emulsion layers has so far precluded reaching a quantitative conclusion. However, the

https://doi.org/10.1021/acs.energyfuels.1c02152
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water that does separate is no longer cloudy, suggesting loss of dispersed TMDD from the initially cloudy aqueous phase.

We wondered if the good synergetic effect of the sparingly soluble TMDD may be due to coating the surfaces of the cell or walls with the chemical, reducing the access of gas or water to the metal surfaces which in turn could inhibit hydrate heteronucleation. However, other sparingly soluble chemicals such as 1-hexanol or 1-octanol showed poor synergy with PVCap, as do a number of film-forming corrosion inhibitor surfactants, so we believe that the powerful synergetic effect of TMSS is related to its structure and not just the low solubility.[19,32,33] In addition, TMDD when tested by itself had a very little effect on the KHI performance giving T_o values only 1.5−2.0 °C lower than using no additive (Table 2).

Although the T_o value is the most important parameter in SCC tests, the T_a value and especially the $T_o - T_a$ value can give a measure of the ability to slow the growth of the nucleated gas hydrates. As seen in Table 2, many solvent synergists not only lower the T_o value but also lower the T_a value even more compared to using the KHI polymer alone. For example, for PVCap, the average $T_o - T_a$ value is significantly greater when good solvent synergists such as iBGE or TMDD are added. The T_o value for the blend of TMDD with iHexOl gave such low T_o values (ca. 3 °C) that rapid hydrate growth giving T_a values was not obtained even at a minimum test temperature of 2 °C. For the blend with added decane, the $T_o - T_a$ value is only 0.6 °C. This is not very high compared to some other synergist blends. However, the subcooling increases as T_o decreases such that it becomes increasingly more difficult to prevent rapid hydrate growth as the thermodynamic driving force (chemical potential) for hydrate formation increases.

3.2. Isothermal KHI Test Results. For further conformation of the powerful synergism of TMDD with PVCap, we carried out a series of isothermal tests (Table 3). We used just 20 mL aqueous solutions and the same SNG for these tests as used in the SCC tests. With no liquid hydrocarbon phase at approx. 68 bar and a test temperature of 6.0 °C, 2500 ppm PVCap formed hydrates before reaching this temperature. Cooling to 6 °C takes about 120 min so that the hold time (t_i) measured from the start of cooling was in the range 80−90 min. iBGE has previously been shown to be a good synergist for PVCap, somewhat better than *n*-BGE.[19] In the isothermal tests at 6 °C, the addition of 5000 ppm iBGE to 2500 ppm PVCap did not have much effect on the hold time (117−148 min), but the time to fast growth (t_a) was considerably longer, 398−509 min.

Tests with 2500 ppm PVCap plus 5000 ppm TMDD were conducted at 4 °C, as we expected the hold times were much higher than those for iBGE based on the SCC test results. When the cells are cooled to 4 °C, the pressure drops to ca. 67 bar. Cooling to 4 °C takes about 155 min. The equilibrium temperature (T_{eq}) is ca. 19.8 °C at this pressure predicted using PVTSim software giving a subcooling (ΔT) of about 15.8 °C. The addition of TMDD to the PVCap increased the hold time to the range 523−826 min, significantly higher than adding iBGE and at 2 °C lower temperature. This indicates the powerful synergism of TMDD. The pressure drop during rapid hydrate growth varied greatly between tests, sometimes dropping to as low as 30 bar.

To confirm the trends from the SCC tests with added decane, we conducted further isothermal tests with added 1 mL of decane as an artificial liquid hydrocarbon phase. The subcooling was reduced by this addition to approximately 15.5 °C calculated using PVTSim software.[29] The same blend of 2500 ppm PVCap with 5000 ppm TMDD now gave much worse performance with hydrates forming in all cells at about the time when a minimum temperature of 4 °C was reached. As with the SCC tests, we believe that the poorer result is due to TMDD partitioning to the decane phase.

The SCC tests with added decane showed that the addition of TMDD still gave a synergetic improvement in performance. Therefore, in order to see the synergy in an isothermal test, we conducted tests with a higher concentration of KHI polymer, 7500 ppm PVCap, with 5000 ppm TMDD. As shown in Table 2, without the TMDD synergist, hydrates form before reaching a minimum temperature of 4 °C. With the synergist and no decane, the average hold time was 398 min. More interestingly, there was no major pressure drop even after 3500 min (nearly 2.5 days). After this time, the total pressure drop was less than 1 bar. This was a major improvement on crystal growth inhibition compared to the synergistic blend with only 2500 ppm PVCap. Vinyl caprolactam-based polymers such as PVCap are known to be good hydrate crystal growth inhibitors. Therefore, at such a small amount of water-to-hydrate conversion, it is possible that the hydrates are still dispersed in the aqueous phase and not agglomerated or deposited.[34,35]

When 1 mL of decane was added to the same system of 7500 ppm PVCap and 2500 ppm TMDD, the hold times decreased relative to the system without decane. This agrees with the SCC tests. The average hold time dropped from 398 to 284 min. This is still significantly better than 7500 ppm PVCap by itself, suggesting that some TMDD was still active in the aqueous phase for a synergetic effect.

4. CONCLUSIONS

The KHI performance of several well-known KHI polymers, PVCap, *N*-vinyl caprolactam/*N*-vinyl pyrrolidone copolymer, and poly(*N*-isopropylmethacrylamide), was significantly boosted by blending with the low-foaming acetylenic diol gemini surfactant TMDD. This was borne out in both SCC and isothermal high-pressure rocking cell experiments. More water-soluble ethoxylated versions of TMDD or the use of 5-MH with a single isobutyl group did not give good synergy. We believe that the low aqueous solubility of TMDD (1700 ppm at 20 °C) and the presence of two isobutyl groups are key features contributing to the synergism.

The addition of decane as a model liquid hydrocarbon phase lowered the synergetic performance of polymer blends with TMDD in both the SCC and isothermal tests. This is probably due to partitioning of TMDD to the hydrocarbon phase. This study highlights the need to choose solvent synergist systems carefully. In future studies, we will be exploring the effect of the added liquid hydrocarbon phase on both KHI polymers and solvent synergists in more detail. We will also explore the effect of a structure I hydrate-forming gas (methane) and salinity with a range of synergist solvents, including other sparingly soluble solvents with structural features similar to TMDD. We predict that solvent synergists that do not significantly partition to the liquid hydrocarbon phase (condensate or oil) should not lose their synergetic effect with KHI polymers as much as more sparingly water-soluble solvent synergists. Thus, just as one can tailor the solubility of a KHI polymer as one of the factors involved in obtaining optimal performance in a given system, this principle also holds for the solvent synergist.

https://doi.org/10.1021/acs.energyfuels.1c02152
Energy Fuels 2021, 35, 15721−15727

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Notes

The authors declare no competing financial interest.

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