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An Investigation of Kinetic Hydrate Inhibitors on the Natural Gas from the South China Sea

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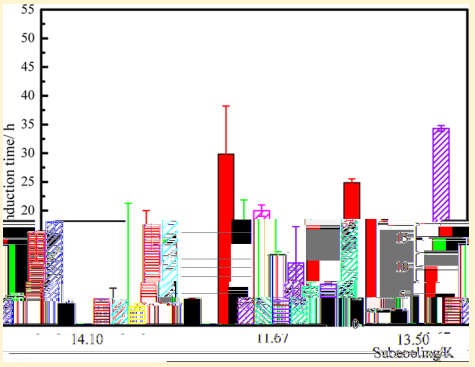
ABSTRACT: We first measured the hydrate equilibrium of two real gases from the South China Sea in the pressure range of 1.85 MPa to 9.32 MPa. Then, three kinetic hydrate inhibitors (poly(*N*-vinyl) pyrrolidone, Inhibex501, and synthesized KHI-HY4) were tested from 275.15 K to 283.15 K and the pressure range from 2 MPa to10 MPa in the case of two real gases under 11.6 K to 14.0 K subcooling. The results show that the maximum subcooling temperature of three hydrate inhibitors increased with the increase of the pressure for the real gases, and hydrate formation induction time increased more than 1.5 times with the inhibitor concentration decreasing for HY4 or Inhibex501 for the real gases at a certain subcooling range. It was believed that each inhibitor has its optimal subcooling for usage in real gas. When the subcooling reached the optimal value, remarkable inhibitory performance could be displayed.



INTRODUCTION

Natural gas hydrates are ice-like structure compounds composed of water molecules encaging guest gas molecules, typically forming at high pressure and low temperature conditions.[1,2] Gas hydrate can form in subsea pipelines when the pipeline fluid containing light hydrocarbons and residual production water is at high pressures (typically 6 MPa to 10 MPa) and low temperatures (around 277 K).[3] Hydrate formation in gas and oil pipelines can lead to pipe blockage and production safety risk.[4−6] Different methods are used to control or prevent gas hydrate formation. According to their different roles, these methods are classified as thermodynamic prevention or as kinetic control. The thermodynamic method mainly points to injecting thermodynamic inhibitors, such as methanol or ethylene glycols or slats, which shift the hydrate phase equilibrium to a lower temperature and a higher pressure zone. However, thermodynamics hydrate inhibitor (THI) usage will generate high operational costs due to large dosages of THI (w = 0.40 to 0.50, x and w represent the mole fraction and mass fraction of additive in the aqueous solution, respectively) needed to inject and retreat. For example, ethylene glycol is usually recovered downstream and recycled. The other problem that cannot be ignored is environmental pollution brought by unrecovered methanol. All of these stimulate the kinetic control method to replace the thermodynamic prevention method. The research of the kinetic control methods has been focused on the kinetic hydrate inhibitors (KHIs). KHIs are usually water-soluble polymers and are effective at about 0.005 to 0.02 mass fraction of the water, which is 1 % to 10 % of ethylene glycol or methanol concentrations to prevent hydrate at similar subcooling. Unlike thermodynamics inhibitors that shift the equilibrium of hydrate, KHIs inhibit the hydrate nucleation and delay the growth of gas hydrate in the pipelines.

The major variety of available KHIs are those polymers based on the 5- and 7-ring *N*-vinyl lactams, such as poly-*N*-vinylpyrrolidone (PVP), and poly-N-vinyl caprolactam (PVCap).[7−14] Many research proved that these KHIs based on lactams have good inhibition effects on tetrahydrofuran hydrate and synthetic natural gas with 2−3 compounds.[15−24] Lou et al.[25] studied Luvicap EG inhibitory performance in THF−NaCl (w=0.035) solution system on the Ball-stop rig apparatus. They found that the ball-stop times of Luvicap EG solutions (w = 0.015 and 0.02) were over 12 h in the subcooling more than 5 K. Linga et al.[26] studied the effect of PVP on the methane/propane (0.905/0.095 mole fraction) gas mixture in the water + silica system at 4.25 MPa and 277.15 K. The results showed that average induction times for PVP (w = 0.005 and w = 0.01) was 146 h and 70.6 h, respectively, in approximate 13 K subcooling, which were far longer than the induction time of no inhibitor samples. Duchateau et al.[27] tested the performance of PVP K30 on a methane (x = 0.98)/propane (x = 0.02) binary gas mixture system. The average induction time was about 8.3 h and range from 1.0 h to 24.0 h in 13.0 MPa and 9.8 K subcooling. Besides, Englezos et al.[28] researched the effect of PVP (M_n = 3.5 kDa) in a simple natural gas mixture system consisting of methane (x = 0.93)/ethane (x = 0.05)/propane (x = 0.02). The solution used was saline solution and saline + heptanes under 7.0 MPa. The results showed that at a cooling rate of 1 K/h in the presence of PVP, the induction time for saline and saline + heptanes solution was

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17.50 h and 17.65 h and corresponding subcooling for the above solution was 14.0 K and 11.5 K. However, the components of a gas mixture from a gas field were more complicated than those in a simple synthetic natural gas mixture, and the performance of the same KHIs between real gas and simple natural gas may display differently. So it is important to study the application of a KHI on a real field gas.

In this paper, we measured the hydrate phase equilibrium condition of two kinds of real gas from the South China Sea gas field. Then, the performance of three KHIs, PVP K90, Inhibex501, and HY4, is tested in two kinds of real gas at 12 K to14 K subcooling.

EXPERIMENTAL SECTION

Materials. HY4 was synthesized by free-radical polymerization of *N*-vinyl-2-pyrrolidone in diethylene glycol monobutyl ether.[29] PVPK90 and Inhibex501 (vinyl caprolactam/vinylpyrrolidone copolymer in butoxyethanol solution (w = 0.5) were commercial KHIs. The materials used in this work, along with their purities and suppliers, are listed in Table 1.The samples of gas A and gas B were simulated gas the composition of which was as same as that of natural gas of South China Sea. Their compositions are shown in Table 2. Distilled water used in all experiments was weighed on an electronic balance with an accuracy of ± 0.1 mg.

Experimental Apparatus. The phase equilibrium measurements were conducted in a high-pressure stainless steel cell with a volume of 300 cm^3 (Hai'an Oil Scientific Research Apparatus Company, China), equipped with a magnetic stirrer to agitate the content inside the vessel. The schematic diagram of the apparatus is shown in Figure 1, and has also been described by Li[30] and Yang et al.[31] in our previous works. The allowable operational temperature and pressure ranges for the vessel were (252.15 to 423.15) K and (0 to 20.0) MPa, respectively. The temperature of the vessel was controlled by a thermostated bath (Huber CC2-K20B).

The inhibitory performance of the KHI on the real gas A and gas B system was carried out in an apparatus[32] consisting of six identical magnetic-stirred steel cells with a volume of 100 cm^3, shown in Figure 2. A high-pressure nitrogen and vacuum pump were used to convey solutions. In both apparatuses, two platinum resistance thermometers (Westzh WZ-PT100) with an accuracy of ± 0.1 K were placed inside vessels to measure the temperatures in the vapor and liquid phases. A pressure transducer (Senex DG-1300) with an accuracy of ± 0.01 MPa was used to measure the internal pressure of vessels. The experimental data were recorded by a data logger (Agilent componendd

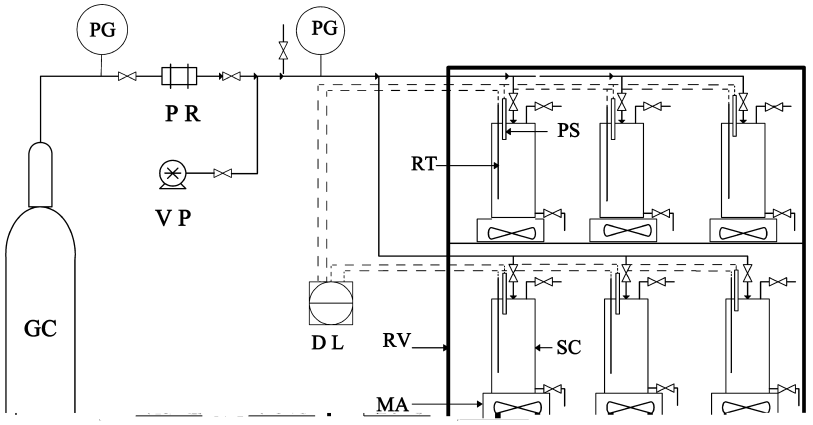

Figure 2. Refrigeretion system of six cells for evaluation of kinetic hydrate inhibitor performance. (GC) gas cylinder; (VP) vacuum pump; (PG) pressure gauge; (PR) pressure regulator; (PS) pressure sensor; (RT) resistance thermometer; (DL) data logger (RV) refrigeration vessel; (SC) steel cell; (MA) magnetic agitator.

was adjusted to (1 to 2) K above equilibrium points at a corresponding pressure in the experiment. Then the temperature of vessel cooled to the set point until the hydrate forms inside. The detailed test procedures are as follows: (1) HY4, PVP K90, and Inhibex501 were dissolved in the distilled water to form 0.01 mass fraction solutions, respectively. (2) A 40 g sample of the prepared solutions was charged into the cell (100 mL) by vacuum pump. (3) The temperature of the cooling bath was set to (1 to 2) K higher than the hydrate phase equilibrium temperature at the desired conditions. (4) Then the cell was loaded with gas A or B to the desired pressure and stirred at 550 rpm. (5) The cell was cooled to the desired temperature.

RESULTS AND DISCUSSION

Hydrate Phase Equilibrium Data. Figure 3 presented the hydrate phase equilibrium curves of gas A + water and gas B + water systems. The experimental data were reported in Table 3. There was a strange phenomenon in which the phase equilibrium curve for the gas A + water system was shifted to the lower pressure or higher temperature zone compared to the gas B + water system, which was opposite to the general knowledge. Common sense tells us that the heavier is the component (C_3H_8 to C_7H_{16} alkane), the lower is the phase equilibrium pressure. For example, the phase equilibrium curves for CH_4 + C_3H_8 gas + water system, CH_4 + 2-methylpropane gas + water system, CH_4 + C_5H_{12}, and the CH_4 + C_6H_{14} gas + water system are all shifted to a lower pressure zone compared with the CH_4 + water system (Figure 3). While in our experiments, the result was opposite. The reason was likely that the dew point of gas B was higher than that of gas A at the same pressure, and the heavy gas in gas B easily condensed into a liquid. Component changes of gas A and B at different pressures and temperatures, which were obtained from Aspen Plus V7.2 software by flash model, were summarized in Table 4 and Table 5. The content of C_4H_{10} to C_7H_{16} alkane condensation (x = 0.0078) for gas B was more than that of gas A (x = 0.007), as shown in Figure 4 and Figure 5. Therefore the molar fraction of CH_4 for gas B increased from 0.8654 to 0.8910, which exceeded the fraction of CH_4 for gas A. Detailed data were also shown in Figure 6. By an analysis of data from a flash model in Aspen Plus V7.2 software, we concluded that the content of C_4H_{10} to C_7H_{16} alkane condensation in gas B was more than that in gas A during the cooling process to obtain

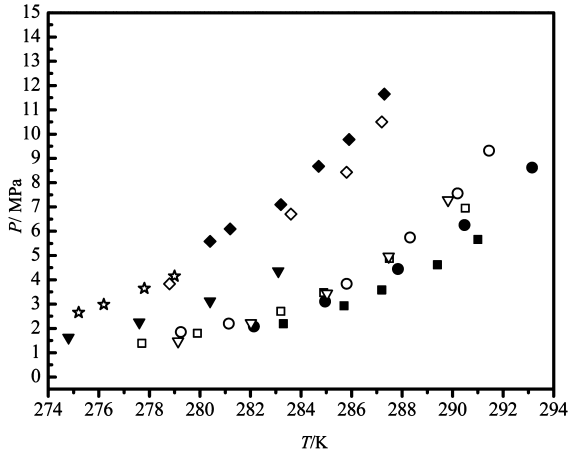

Figure 3. Three-phase coexistence curves of two hydrate-forming systems studied in this work: ●, gas A + water system; ○, gas B + water system. The data of ◆, CH_4+water; ▼, CH_4+C_3H_8 gas + water; □, CH_4+ 2-methylpropane gas + water; ☆, CH_4+C_5H_{12} gas + water system; ◇, natural gas 1 + water system; and ■, natural gas 2 + water system were from the ref 2. The data of ▽, CH_4 + C_6H_{14} gas + water system were taken from the ref 35. The phase equilibrium curves for CH_4+C_3H_8 gas + water system, CH_4+ 2-methylpropane gas + water system, CH_4+C_5H_{12} gas + water system, and the CH_4 + C_{6+}

Table 4. Component Changes of Gas A at Various Pressures and Temperatures

	$x \cdot 10^{-2}$									
condition	CH_4	C_2H_6	C_3H_8	CO_2	N_2	2-methyl propane	C_4H_{10}	1-methyl butane	C_5H_{12}	C_6H_{14}
9 MPa, 298 K	87.154	3.602	1.431	5.733	0.410	0.290	0.300	0.100	0.030	0.950
8 MPa, 293 K	87.245	3.600	1.430	5.730	0.410	0.290	0.300	0.100	0.030	0.950
7 MPa, 288 K	87.344	3.596	1.418	5.737	0.411	0.280	0.290	0.094	0.027	0.796
6 MPa, 283 K	87.594	3.588	1.400	5.743	0.413	0.275	0.277	0.086	0.025	0.598
5 MPa, 278 K	87.786	3.584	1.384	5.750	0.414	0.266	0.265	0.078	0.022	0.450
4 MPa, 274 K	87.893	3.585	1.378	5.756	0.414	0.262	0.257	0.073	0.019	0.361

Table 5. Component Changes of Gas B at Various Pressure and Temperature

	$x \cdot 10^{-2}$ (mole fraction)										
condition	CH_4	C_2H_6	C_3H_8	CO_2	N_2	2-methyl propane	C_4H_{10}	1-methyl butane	C_5H_{12}	C_6H_{14}	C_7H_{16}
9 MPa, 298 K	88.258	5.171	1.715	3.138	0.041	0.330	0.418	0.168	0.111	0.102	0.547
8 MPa, 293 K	88.522	5.161	1.689	3.141	0.041	0.318	0.398	0.153	0.099	0.082	0.395
7 MPa, 288 K	88.743	5.153	1.664	3.145	0.041	0.305	0.377	0.137	0.088	0.064	0.280
6 MPa, 283 K	88.921	5.149	1.642	3.149	0.041	0.293	0.358	0.123	0.077	0.050	0.195
5 MPa, 278 K	89.054	5.152	1.625	3.155	0.041	0.282	0.339	0.109	0.067	0.038	0.135
4 MPa, 274 K	89.102	5.169	1.625	3.162	0.041	0.277	0.330	0.101	0.061	0.031	0.099

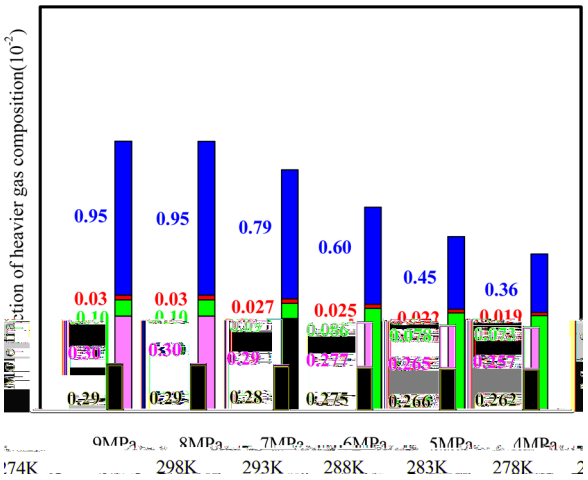

Figure 4. Composition change of heavier components from gas A at different pressure and temperature: (blue) C_6H_{14}; (red) C_5H_{12}; (green) 1-methylbutane; (pink) C_4H_{10}; (brown) 2-methylpropane.

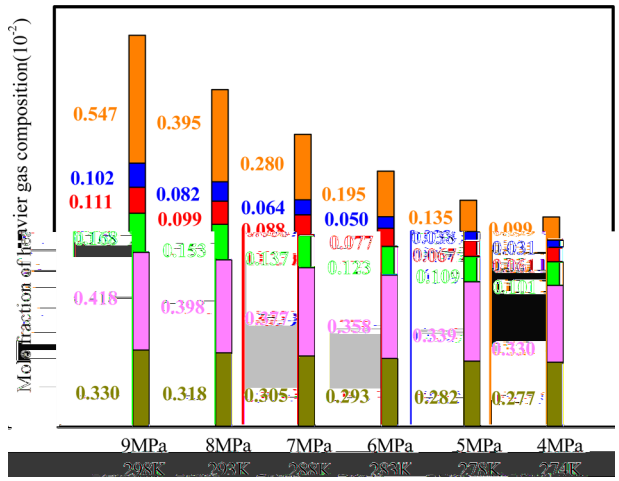

Figure 5. Composition change of heavier components from gas B at different pressure and temperature: (orange) C_7H_{16}; (blue) C_6H_{14}; (red) C_5H_{12}; (green) 1-methylbutane; (pink) C_4H_{10}; (brown) 2-methylpropane.

adequate hydrate in the autoclave. This caused gas A to contain heavier constituents than gas B and formed hydrate more easily. The result was well consistent with those of Jensen et al.[36] On the other hand, the hydrate phase boundary for gas A + water, gas B + water, and natural gas 1[2] and natural gas 2[2] system also proved the above conclusion. The ranking of the content of heavy gas (C_3H_8 to C_7H_{16} alkane) in four different systems was natural gas 2 > gas A > gas B > natural gas, and so the slopes of the $P-T$ curve of the gas A + water system and gas B + water system were in the middle of natural gas 1 and natural gas 2.[2]

Hydrate Inhibitor Performance Tests. *S bcooling for KHI* . Kinetic hydrate inhibitors (KHIs) have been always limited by their attainable subcooling in field applications and generally ineffective at high subcooling (>10 K). So subcooling was a key parameter to evaluate the hydrate inhibitors. Hence, various cooling methods were used to test subcooling (ΔT) that they could achieve under a certain pressure. In this paper, the step-cooling method was used to seek the maximum subcooling (ΔT) of HY4, PVP K90, and Inhibex501 in gas A or B + water system. The maximum subcooling (ΔT) was defined

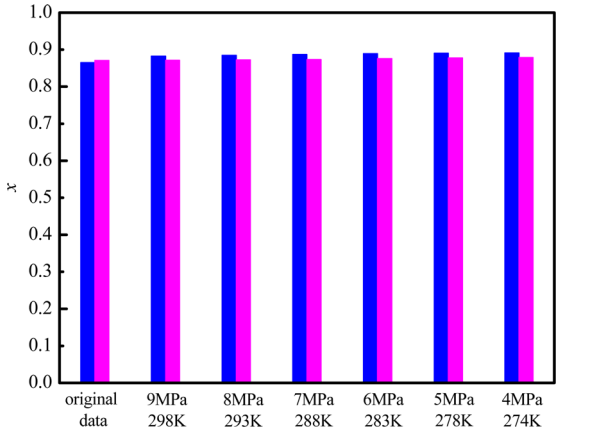

Figure 6. Composition change of CH_4 from gas A and B at different pressure and temperature: (pink) gas A; (blue) gas B; x is mole fraction.

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as the highest temperature difference between the gas hydrate phase equilibrium temperature and hydrate formation temperature, which the inhibitor can tolerate in tests. As a representative, the change of pressure and temperature in testing the subcooling of HY4 in gas B + water system was shown in Figure 7. All results of maximum ΔT for those KHIs

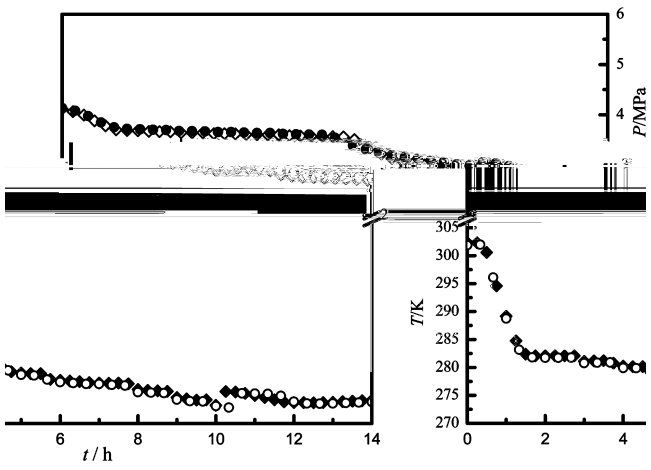

Figure 7. Data from the step cooling test with HY4 at 0.01 mass fraction dosage, in the case of the 4.3 MPa-based two measurements. At the beginning of the experiment, the cell was loading B gas to 4.3 MPa at 303.15 K, and the corresponding hydrate phase-equilibrium temperature was about 286.16 K. In the first cooling stage, the temperature cooled from 303.15 to 286.16 K in 1 h. Then, the temperature of the cell was cooling at a 1 K·h^{-1} rate from 286.16 K to 273.15 K: ○, T_1; ◆, T_2; ●, p_1; ◇, p_2.

Table 6. Maximum Subcooling That Can Be Achieved in KHIs Testing

		T/K		
solution	p/MPa	HY4	PVP K90	Inhibex501
A system + water	8.65	20.0	20.1	20.5
	6.00	18.0	17.9	17.5
B system + water	4.30	13.0	12.7	13.5
THF[23]		8.2	2.0	5.2
methane/ethane)/propane + saline + heptanes[28]	7.00		11.5	

in the gas A and B systems were summarized in Table 6. The maximum subcooling temperature of HY4, PVP K90, and Inhibex501 increased with the increase of the pressure, because for multicomponent systems, the driving force ($\Delta G/RT$) of hydrate formation decreases by increasing the pressure, up to 20 MPa.[37] Interestingly, their subcooling all exceed 10 K, even the maximum subcooling exceed to 20 K in 8.65 MPa, which is more than the literature value obtained from the testing in THF solutions or simple gas mixture.

The Ind c ion Time for KHI . The induction time was used to judge inhibitory performance of KHIs in certain subcooling, and good KHIs had a long induction time. The induction time (t_i) is defined as the time from t_b (start time of cooling) to t_0 (the time of first detectable hydrate formation). At least two experiments were carried out at one condition with the same polymer in order to reduce stochastic results. Figure 8 displayed typical curves of pressure and temperature versus time recorded

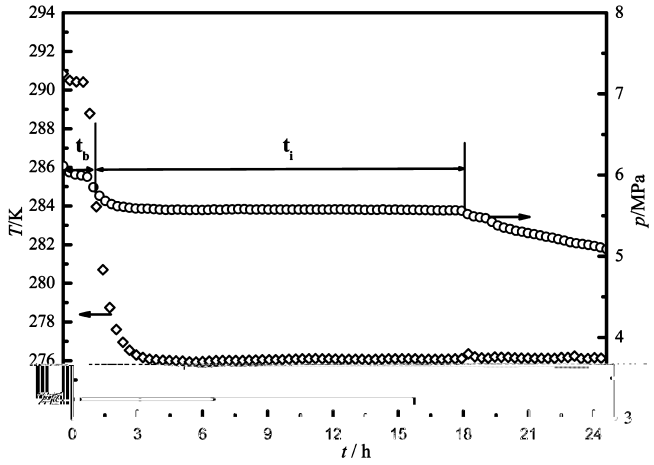

Figure 8. Data from the isothermal cooling test with Inhibex501 at 0.01 mass fraction dosage, in the case of 6.0 MPa and 14.1 K subcooling. At the beginning of experiment, the cell was loading gas A to 6.0 MPa at 291.15 K and corresponding hydrate phase-equilibrium temperature is 290.15 K. ◇, T; ○, p.

in an experimental run (Inhibex501 solutions in the gas A system). As shown in Figure 8, at the beginning of cooling process, the experimental pressure drops with the temperature drop in a closed system, and the pressure dropped during the stable period of P and T indicated hydrate began forming in the cell. On the other hand, hydrate formation is an exothermic process which can be seen by the spike in temperature at the beginning of the growth period, which also could be seen in Figure 8. The analysis for t_b and t_i was displayed in Figure 8.

As expected, the induction time for the system with no inhibitor was significantly lower than those with KHIs at the same experimental conditions. The time for first detectable hydrate formation (t_0) and induction time were summarized in Table 7, and the average induction time for all polymers used in the experiments was also illustrated in Figure 9. In the case of 8.65 MPa and 11.67 K subcooling, PVP K90 gave better performance than HY4, whereas in high subcooling (13.5 K), synthesized HY4 gave a significantly higher average t_i value (29.86 h) than the PVP K90. It may show that HY4 was more suitably applied in higher subcooling conditions. Compared the inhibitory performance of HY4 and Inhibex501 at 14.1 K subcooling, we found that HY4 had a longer induction time than Inhibex501 at both dosages (w = 0.01 and 0.015) and the system with the addition of HY4 (w = 0.01) had no observed hydrate formation in more than 24 h. On the other hand, the effect of concentration on hydrate formation at the same subcooling was explored by adding 0.01 and 0.015 mass fraction of KHIs. The results indicated that hydrate formation induction time increased more than 1.5 times as the concentration decreased for HY4 or Inhibex501. It was speculated that diethylene glycol monobutyl ether and butoxyethanol as solvent introduced to HY4 and Inhibex501 enhanced the solubility of the gas molecules in water and the diffusivity of gas molecules through the hydrate boundary. This speculation was consistent with Zepra's theory.[38] So with an increased concentration of the KHIs, the limitation mass-transfer became small and induction time was advanced. The anomaly of the subcooling effect on induction time was discovered in a real gas system and induction time was not reduced with increasing subcooling in the specific scope, which was different from the conventional point that the induction

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time decreased with the increasing subcooling. For HY4, induction time increased from 14.75 h to 31.61 h at 0.01 mass fraction when subcooling increased from 11.67 K to 13.5 K. While the subcooling increased to 14.1 K, the induction time suddenly became shorter than 26.0 h. We deduced that each inhibitor has its optimal subcooling for usage. Only when the subcooling reached the optimal value, could remarkable inhibitory performance be displayed. For example, when subcooling was 13.5 K and 15.0 K[39] for the PVP K90 (w = 0.01) system, the induction time was 17.51 h and more than 20.0 h, respectively; when the subcooling increased to 23.47 K, the induction time suddenly became shorter than 4.0 h.[40] Unlike that for PVP K90, the induction time for Inhibex501 was delayed with the subcooling range from 8.6 K to 14.7 K.

To further elucidate the inhibitory performance of HY4 and commercial PVP K90 and Inhibex501 in the gas of South China Sea, we carried out several reduplicative tests in gas B, and the experiments were running under around 4.0 MPa and 13.0 K subcooling. The results showed that the induction time (t_i) for HY4 and Inhibex501 at a dosage of 0.01 mass fraction is similar, about 9.5 h, while PVP K90 showed slight worse performance than this in approximately the same conditions, and the t_i was 8.4 h. On the basis of these findings we considered that HY4 to be superior in stern conditions, lower subcooling, and higher pressure areas.

CONCLUSION

Hydrate formation conditions of two gases from South China Sea gas field were measured in a high-pressure stainless steel cell with a temperature range of (279.25 to 293.15) K and

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Notes

The authors declare no competing financial interest.

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