Effect of the combination of hydrophilic nano-SiO$_2$ and gaffix VC-713 polymer on CH$_4$ hydrate formation: Insight from the experimental study

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Abstract. In this paper, the effect of the combination of hydrophilic nano-SiO$_2$ with a particle size of 80 nm and gaffix VC-713 polymer (VC-713) on their hydrate inhibition was investigated at 4.0°C and 6.0 MPa, and the underlying influence mechanism was analysed by a multiple scales of the meso-structural observation experiments. Experimental results indicated that the combination doesn’t exhibit any synergistic inhibition effect on the formation of CH$_4$ hydrate, but it weakens the hydrate inhibition abilities of both components. Moreover, with the increase of the VC-713 content to 0.75 wt% and 1.00 wt%, the inhibition of hydrophilic nano-SiO$_2$ completely disappears.

1. Introduction
As a potential alternative energy source, drilling operations are an important part of natural gas hydrate exploration and exploitation [1-3]. In order to maintain the borehole stability and safety, The gas hydrate-bearing sediment (GHBS) drilling operations are performed under overpressure conditions, and drilling fluid would permeate into the GHBS due to the pressure difference [4]. Research work has demonstrated that to eliminate the negative effects and keep the borehole stable, drilling fluid loss should be minimized, and the application of nanoparticles is an effective way to reach such goal [5]. Wang et al has reported that 4.0 wt% of hydrophilic nano-SiO$_2$ with a particle size of 80 nm can effectively inhibit the formation of hydrates in a simulated drilling fluid under different driving force conditions [6]. Liu et al has reported that the addition of 2% hydrophilic nano-SiO$_2$ into the hydrate drilling fluid system can not only optimize the properties such as rheology, depressing filter loss, and shale inhibition, but also ensure the hydrate inhibition of the low-cost drilling fluid system [7].

Although it has been reported that the application of hydrophilic nano-SiO$_2$ in hydrate drilling fluids has achieved some progresses, these studies just involved simple nano-fluids and mature drilling fluid systems. In addition, the effect of the composite of hydrophilic nano-SiO$_2$ and hydrate kinetic inhibitors on their hydrate inhibition was not revealed, and the underlying influence mechanism was also not explained. In this study, the combination was prepared using 4.0 wt% of hydrophilic nano-SiO$_2$ with a particle size of 80 nm (studies have reported that hydrophilic nano-SiO$_2$ under this condition exhibit the optimum inhibitory effect on methane hydrate formation [8]) and the hydrate kinetic inhibitor VC-713 with good inhibition and widely used (the concentrations of VC-713 were...
0.25 wt%, 0.50 wt%, 0.75 wt%, and 1.00 wt%). In addition, the above issues were investigated in detail by multiple perspectives using various methods, including simulations of methane hydrate formation and meso-structural observations of simulated drilling fluid. The results obtained from this study can provide important reference values for the industrial applications of nano materials for hydrate field and the development on new types of conventional oil as well as gas drilling fluid and hydrate drilling fluid systems.

2. Experimental section

2.1. Materials and instruments

The purity of CH₄ gas used in this work is 99.9%, provided by Wuhan Niuruide Trading Co., Ltd., China. Hydrophilic silica, grain size 80 nm, provided by Qinhuangdao Nano products Co., Ltd., China. VC-713 is produced by International Special Products (ISP) Co., Ltd., America. Ultrapure water (abbreviated as UPW) resistivity more than 18.25 MΩ·cm is made up of a type UPW-S Millipore unit. In order to uniformly disperse the hydrophilic nano-SiO₂ in simulate drilling fluids, high speed stirring at 20000 r/min was used in our experiments.

The schematic of the experimental apparatus for hydrate formation is shown in figure 1. In order to conduct meso-structure observations, initially the lyophilized samples from simulate drilling fluid were prepared using the Four-Ring LGJ-10D freeze dryer. Then, the samples were observed by the Quanta 200F field emission scanning electron microscope (SEM).

![Figure 1. Schematic of the experimental setup.](image)

2.2. Methodology

2.2.1. Experiments on CH₄ hydrate formation. Hydrate formation process was simulated by constant volume method [9]. To ensure the repeatability of the experiments, each experiment was repeated three times. The specific experimental steps are as follows.

- Use a clean 650 ml reactor and check its tightness.
- The liquid sample of 250 mL was injected into the reactor and vacuum continuously for 10 min. CH₄ gas was injected into the buffer tank until the pressure reached 10.0 MPa. Then turn on the temperature control system to lower the temperature. To avoid the aggregation and precipitation of the hydrophilic nano-SiO₂, the liquid sample was stirred at a speed of 300 r/min.
- After the temperature of the system was stabilized at 4.0°C, the CH₄ gas was injected into the reactor through the upper air inlet until the pressure reached 6.0 MPa. Then, the stirring speed was increased to 600 r/min and the monitoring software was turned on to collect the temperature and pressure data (the frequency of data acquisition is one time per 2 seconds).
2.2.2. Observing the mesoscopic structure. It has been reported that the meso-structural features of simulate drilling fluid can analyse its underlying influence mechanism of hydrate formation [10, 11]. The experimental procedure is shown as following:

- Use the dropper to take a small amount of simulated drilling fluid, drop onto a mica film, and place it in liquid nitrogen for 2.0 min.
- The frozen sample was lyophilized in a freeze-drier for 20.0 h.
- The mesoscopic structure of the sample was observed by SEM after preparation.

3. Results

3.1. Evaluation of the hydrate inhibition

3.1.1. Data processing. During the evaluation of hydrate inhibition, the induction time, amount and rate of hydrate formation will be comprehensively analyzed. Taking the curves of temperature and pressure during the formation of hydrates in UPW and the nano-fluid with concentration of 4.0 wt% as an example (figure 2), the induction time $t_1$, the stopping time of hydrate formation $t_2$, the starting pressure $P_1$ and the stopping pressure $P_2$ of hydrate formation can be obtained.

![Figure 2. Variation in temperature and pressure with time for each experiment.](image)

Since the guest gas is high-purity CH$_4$, its consumption represents the formation amount of hydrates. Therefore, the amount of hydrate formation can be calculated using the following equation [12-14]:

$$
\Delta n = \left( \frac{P_1}{Z_1} - \frac{P_2}{Z_2} \right) \cdot \frac{V}{RT}
$$

(1)

where $\Delta n$ is the amount of methane consumption, mol; $R$ is gas constant, equal to 8.31441 J/(mol·K); $T$ is gas temperature, K; $V$ is gas volume, m$^3$; and $Z_1$, $Z_2$ are the initial compressive factor and final compressive factor, respectively. The compressive factor can be calculated as follows [15]:

$$
Z = 1 + \left( A_1 + \frac{A_2}{T_{pr}} + \frac{A_3}{T_{pr}^3} \right) + \left( A_4 + \frac{A_5}{T_{pr}} \right) \rho_r^2 + \left( \frac{A_6}{T_{pr}} \right) \rho_r^3 - \frac{A_7}{T_{pr}^3} \rho_r^7 (1 + A_8 \rho_r^2) \exp(-A_9 \rho_r^2)
$$

(2)

where $A_i$ is given parameters ($A_1$=0.31506237, $A_2$=-1.0467099, $A_3$=-0.57832729, $A_4$=0.53530771, $A_5$=-0.61232032, $A_6$=-0.10488813, $A_7$=0.68157001, $A_8$=0.68446549) [14]; $P_{pr}$ is comparative pressure; $T_{pr}$ is comparative temperature; $\rho_r$ is methane comparative density. $P_{pr}$, $T_{pr}$ and $\rho_r$ are calculated as follows:
\[ P_p = \frac{P}{P_c}, \quad T_p = \frac{T}{T_c}, \quad \rho_i = 0.27\left(\frac{P_p}{ZT_p}\right) \]  
(3)

where \( P \) is methane gas pressure, MPa; \( P_c \) is critical pressure of methane gas, about 4.60 MPa [12]; \( T \) is methane temperature, K; \( T_c \) is critical temperature of methane gas, about 191.11 K [12]. Substituting the experimental data into equations (1), (2), and (3), the consumption of methane gas can be calculated.

The rate of hydrate formation can be characterized by the methane consumption per unit time, which is the average consumption rate of methane between the period of starting and stopping hydrate formation. The calculation formula can be deduced based on equation (1) and is expressed as follows.

\[ v = \frac{\Delta n}{(t_2 - t_1)} \]  
(4)

where \( v \) is the average consumption rate of gas, mol/min.

3.1.2. Data obtained. According to the various parameters shown in figure 2, when 4.0 wt% of hydrophilic nano-SiO\(_2\) with a particle size of 80 nm was uniformly dispersed in the system, the induction time of CH\(_4\) hydrate formation can be calculated to be prolonged by 70.4%, the formation amount decreased by 9.7%, and the formation rate decreased by 14.3% compared to the UPW experiment (induction time of CH\(_4\) hydrate formation was 9.06 min; gas consumption was \( \sim 0.51 \) mol; and average gas consumption rate was \( \sim 0.88 \times 10^{-3} \) mol/min). Results indicated that hydrophilic nano-SiO\(_2\) effectively inhibits the nucleation and growth of hydrates under this experimental condition.

According to the method mentioned in Section 3.1.1, the induction times, amounts and rates of CH\(_4\) hydrate formation in the VC-713 aqueous solutions with concentrations of 0.25–1.00 wt% and the groups of fluids with the addition of hydrophilic nano-SiO\(_2\) can be calculated (figure 3). It can be known from figure 3 that the addition of hydrophilic nano-SiO\(_2\) can decrease the induction times for the formation of CH\(_4\) hydrate and increase the formation rates compared to the CH\(_4\) hydrate formation in VC-713 aqueous solutions with different concentration. When the additions of VC-713 in the nano-fluids were 0.25 wt% and 0.50 wt%, the amounts of the formed CH\(_4\) hydrates decreased, but the amounts were slightly greater than those in the nano-fluids prepared with hydrophilic nano-SiO\(_2\) and UPW under the same experimental conditions. The addition of a kinetic inhibitor will not change the amount of hydrate formation [9]. Therefore, with the increase of the content of VC-713 in the tested fluid samples, the inhibition ability of hydrophilic nano-SiO\(_2\) on the hydrate formation is gradually weakened. With the VC-713 content being greater than or equal to 0.75 wt%, the inhibition effect of hydrophilic nano-SiO\(_2\) was completely lost.

\[ \text{Figure 3. Hydrate formation (a) induction time, (b) amount, and (c) rate in each experiment.} \]

3.2. Mesoscopic structural characteristics of the system

The meso-structural characteristics of the freeze-dried samples from two groups of fluids (i.e., UPW + 1.00 wt% VC-713 and UPW + 1.00 wt% VC-713 + 4.0 wt% nano-SiO\(_2\), respectively) observed under
different magnifications are shown in figure 4. Using 1.00 wt% of the VC-713 aqueous solution, hydrated VC-713 molecular aggregates were observed as thin rods (diameter of 0.5–1.0 μm) and smooth thin sheets (thickness of ~0.5 μm and diameter of 40–100 μm), comprising a skeleton structure with a dense, complex spatial distribution (figures 4(a), 4(b), and 4(c)). With the addition of 4.0 wt% of hydrophilic nano-SiO$_2$, the hydrophilic characteristic of hydrated VC-713 molecules, small-sized nanoparticles and nanoparticle aggregates adhered to the surface of the skeleton structure, clearly changed the original morphology and spatial structure of the hydrated VC-713 molecular aggregates. The diameter of the thin-rod-like hydrated molecular aggregates slightly increased (around 1.0–3.0 μm), while the amount of thin-sheet-like hydrated molecular aggregates dramatically decreased with the increase of the thickness to 1.5–3.0 μm and decrease of the diameter to 30–70 μm.

4. Analysis and discussion

After uniformly dispersing 4.0 wt% of hydrophilic nano-SiO$_2$ with a particle size of 80 nm in UPW, because of its hydrophilic functional groups on the surface, water molecules near the nanoparticles were bound, and the formation of a cage-like structure from water molecules was inhibited, thereby prolonging the induction time of hydrate formation and decreasing the formation rate of hydrate. Moreover, the water molecules wetted on the hydrophilic nano-SiO$_2$ surface further formed a water film layer, which did not involve in the hydrate formation, leading to the decrease in the amount of methane hydrate formation (figure 5(a)) [6,8]. Compared to the effect of the hydrate inhibition between hydrophilic nano-SiO$_2$ and VC-713, the hydrate inhibition of VC-713 was considerably better than that of hydrophilic nano-SiO$_2$. Hence, the inhibition effect on methane hydrate formation is dominated by VC-713 under the condition of the tested fluid sample containing hydrophilic nano-SiO$_2$ and VC-713. On the other hand, hydrophilic nano-SiO$_2$ played a marginal role in decreasing the amount of the formed methane hydrate with a relatively low amount of VC-713 (e.g., 0.25 wt% and 0.50 wt%, figure 5(b)).

Due to the addition of hydrophilic nano-SiO$_2$ into the VC-713 aqueous solution, hydrophilic nano-SiO$_2$ adhered to the surface of hydrated VC-713 molecular aggregates and inhibited the migration of hydrated VC-713 molecules (figure 4). Since VC-713 inhibited the nucleation and growth of hydrates via the adsorption of the unclosed cage-like structure on water molecules and the formed hydrate crystalline particles [16,17]. Thus, the inhibition of the migration of hydrated VC-713 molecules by hydrophilic nano-SiO$_2$ possibly weakened the inhibition ability of VC-713 to the nucleation and
growth of hydrates, leading to the decrease of the induction time for methane hydrate formation during the experiment and the increase of the formation rate (figure 3). Meanwhile, lactam-containing polymers (e.g., polyvinyl pyrrolidone and VC-713) exhibit a strong film-forming property [17]. Because of the addition of high contents of VC-713 in the fluid samples (i.e., 0.75 wt% and 1.00 wt%), hydrophilic nano-SiO$_2$ uniformly dispersed in the system was possibly wrapped by VC-713, which was similar to the wrapping mechanisms of polyvinyl pyrrolidone and VC-713 on hydrate crystalline particles. Therefore, the surface of hydrophilic nanoparticles cannot form a water film that does not participate in the formation of hydrate (figure 5(c)). This result in turn leads to hydrophilic nano-SiO$_2$ not being able to decrease the hydrate formation amount.

![Figure 5. The possible mechanism.](image)

5. Conclusions and prospects
In this study, the effect and its mechanisms of the combination of hydrophilic nano-SiO$_2$ and VC-713 on their hydrate inhibition was discovered based on the observation of the meso-structural characteristics of the freeze-dried simulated drilling fluids. The results prove that the adsorption and wrapping effect occurred between hydrophilic nano-SiO$_2$ and VC-713 owing to their hydrophilic characteristic and the film-forming property of VC-713, thereby leading to weakened hydrate inhibition of VC-713. Moreover, with the increasing VC-713 content, the hydrate inhibition of hydrophilic nano-SiO$_2$ decreased. When the concentration of VC-713 is greater than or equal to 0.75 wt%, the hydrate inhibition of hydrophilic nano-SiO$_2$ completely disappeared. Hence, the combination of hydrophilic nano-SiO$_2$ and VC-713 does not exhibit a synergistic inhibition effect on the formation of CH$_4$ hydrate, but instead, it weakens the hydrate inhibition ability of each component. This study provides an important research idea for the development of conventional oil as well as gas drilling fluid and natural gas hydrate drilling fluid systems.

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