Synthesis of Chitosan Derivatives and Their Inhibition Effects on Methane Hydrates

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Abstract: In recent years, the study of natural polymer products such as methane hydrate inhibitors has attracted more and more attention in the scientific research field. In order to achieve environmentally friendly and economical methane hydrate inhibitors with high activity, four chitosan derivatives were successfully synthesized and their methane hydrate inhibition effects were compared with chitosan (CS) and carboxymethyl chitosan (CMCS). Under the conditions of 6 MPa, 1 °C and 400 rpm, the induction time of methane hydrate was prolonged by 7.3 times with the addition of 0.1 wt% CS. It was found that chitosan with high hydrophobicity could effectively prevent methane gas from entering the water solution and reduce the driving force of methane hydrates, resulting in the extension of hydrate induction time. The hydrate inhibition effect of CMCS could be improved by the introduction of hydroxypropyl-3-trimethylamine and N-2-hydroxypropyl-3-isooctyl ether groups based on the enhancement of the molecular hydrophobicity. At the same time, the introduction of the trimethyl quaternary ammonium group increased the ion content in the aqueous solution, which further inhibited the nucleation and growth of methane hydrates. This work is supposed to serve as an inspiration for the further research and development of green kinetic hydrate inhibitors with high-efficiency.

Keywords: methane hydrate; chitosan; derivatives; kinetics hydrate inhibitors

1. Introduction

Compounds composed of single or several gas molecules (e.g., nitrogen, carbon dioxide and hydrogen) and water molecules are called gas hydrates. Methane hydrate (mCH₄·nH₂O) is a typical gas hydrate [1,2]. As a combustible clean energy, methane hydrate is mostly distributed in permafrost, deep sea and polar regions in solid crystal or viscous flow state [3,4].

In the process of methane transportation and extraction, the high pressure, low temperature and moisture conditions inside the pipeline can cause methane to form gas hydrates, thereby blocking the pipeline. Once a hydrate block forms, it will not only increase industrial costs, but easily cause major safety accidents such as explosions [5,6]. Therefore, it is imminent to inhibit the formation of methane hydrate in the pipeline. At present, there are physical and chemical methods to solve the problem at home and abroad. In theory, heating, depressurization and removing water could solve the hydrate blockage problem by changing the hydrate formation conditions to inhibit the formation of methane hydrate. However, physical methods not only consume high costs, but have actual potential safety hazards, and it is difficult for factories to meet the theoretical requirements [7]. Chemical methods, including the addition of thermodynamic inhibitors (THIs) and low-dose hydrate inhibitors (LDHIs) to the system, were thought to be potential method to inhibit the hydrate formation [8].

Thermodynamic inhibitors (e.g., methanol, glycol, sodium chloride and potassium chloride) could generally achieve the purpose of inhibiting the formation of hydrates by
changing the thermodynamic conditions for hydrate formation [9]. Nguyen studied the effect of sodium halide on methane hydrate in a gas–liquid environment. The experimental results showed that sodium halide had a dual inhibitory effect on hydrates formation. Low or high concentrations of salt solution reduce the hydrate growth rate; however, the inhibition effect is weakened within the certain range of concentration [10,11]. Vatani et al. calculated the effect of methanol and ethylene glycol as methane hydrate inhibitors by molecular dynamics simulation, and found that 80% methanol and 70% ethylene glycol could achieve a better hydrate inhibition effect [12,13]. It can be seen from the above that thermodynamic hydrate inhibitors need to be added in large quantities to exert the hydrate inhibition effect, which will increase the industrial cost and seriously pollute the marine environment.

Low-dosage hydrate inhibitors, including kinetic hydrate inhibitors, require only 1% to significantly inhibit formation, which will reduce costs and environmental pollution observably. The typical kinetic hydrate inhibitors include polyvinylpyrrolidone (PVP), poly(N-vinylcaprolactam) (PVCap) and other polymers. Posteraro studied the effects of pressure, temperature and molecular weight of PVP on methane hydrate inhibition and found that PVP40 showed the best inhibition performance at 277.1 K and 6282 KPa, reducing the initial hydrate growth rate by 99.3% [14]. The stronger hydrophobic tendency and superior methane hydrate inhibition potential of PVCap were also discovered by Rajput [15]. Cheng and Li et al. studied the inhibition effect of PVP-A on methane hydrate in deionized water, and found that PVP-A had a significant effect on solid–liquid interface and when used in combination with methanol [16,17]. Foroutan also confirmed the excellent hydrate inhibition effects of kinetic hydrate inhibitors [18]. Here are structures of PVP, PVCap and PVP-A (Figure 1). Based on the above researches, amide-based polymers are recognized as effective kinetic hydrate inhibitors.

These well-known kinetic hydrate inhibitors (e.g., PVP, PVCap and PVP-A) have a certain hydrate inhibitory effect; however, poor biodegradability and high cost turn into their disadvantages. Therefore, more and more natural polymers with high biodegradability have been studied as methane hydrate kinetic inhibitors in recent years, such as protein [19], starch [20,21] and pectin [22], which have a certain inhibitory effect in the formation of methane hydrate. Zeng et al. used antifreeze protein (AFPs) in place as a hydrate kinetic inhibitor and demonstrated that AFPs reduced the hydrate memory effect effectively and prolonged the hydrate induction time by triple (56 versus 179 min) [19]. Talaghat studied the inhibitory effects of oxidized starch and PVP on hydrate formation under 1–5 MPa in the 75% methane—25% propane system. The results showed that the induction time at 277.15 K, 5 MPa of oxidized starch was 5.6-fold (2.3 h) longer than that of PVP [20]. Idress et al. researched cassava peel as an inhibitor of methane hydrate kinetics and found that cassava peel can also achieve similar inhibitory effects as the commercial inhibitor PVP [21].
The above research results showed that natural kinetic hydrate inhibitors had similar or even better effects than amide-based inhibitors.

Figure 2 showed the molecular structures of three natural methane hydrate kinetic inhibitors. Hydrate kinetic inhibitors with hydrophobic hydroxyl groups have excellent hydrate inhibition effect. Bui studied the influence of a surfactant grafted with hydrophilic/hydrophobic groups on the inhibition effect of methane hydrate by molecular simulation. The results showed that the inhibition effect of this inhibitor was significantly improved by grafting hydrophobic groups [23]. Rajput studied the effect of PVA copolymers as hydrate inhibitors. The results showed that when poly(2,3,4,5,6-pentafluorostyrene) (PPFS) with strong hydrophobicity was grafted on PVA, the inhibitory effect was better than that of poly(styrene) (PS) with poor hydrophobicity [24].

Figure 2. Molecular structures of natural methane hydrate kinetic inhibitors (starch, guar gum and chitosan).

In general, hydrate formation process in water–methane system is divided into four stages: I. gas dissolution stage, II. induction stage (generate clathrate nucleus), III. growth stage (hydrate growth) and IV. equilibrium [25]. Figure 3 showed the pressure curve of the methane clathrate formation process in theory in pure water. The mechanism of hydrate formation in the systems with inhibitors is not clear at present. However, an almost united mechanism involves two strategies. One is a strategy in which the nitrogen and oxygen atoms of the inhibitor molecule form hydrogen bonds (H-bonds) with the water molecule or clathrate cage [26]. In other words, the inhibitor molecule is adsorbed on the surface of the hydrate crystal nucleus and then methane molecules are prevented from entering and filling the cages. The another one is the aggregation effect, which is related to the hydrophobic properties of the inhibitors, and additives will cover the gas–liquid interface and block the gas–liquid channel [27,28]. Larsen’s study showed that kinetic hydrate inhibitors adsorbed on active sites of the hydrate surface by occupying the surface of hydrate nuclei [29], while Kuznetsova believed that the inhibitor molecules would form a polymer layer, the gas–liquid mass transfer was blocked, the phase migration of water molecules and guest molecules was slowed down, and the hydrate growth was inhibited [30]. In any case, these processes take place in the II stage.
As one kind of alkaline polysaccharide in nature, chitosan extracted from the cell wall of algae and fungi have the properties of rich content, low cost and little impact on the environment and could be a good candidate for inhibiting methane hydrate formation. Wan et al. and Xu et al. proved that chitosan is an excellent inhibitor of methane hydrate kinetics [22,31]. Farhadian found that sulfonated chitosan was a highly efficient green hydrate inhibitor with a high cloud point [32]. However, the effects of chitosan and its derivatives on hydrate inhibition are still unknown. Therefore, it is of great significance to study the inhibitory effect of chitosan and its derivatives on methane hydrate for the development of green and environmental protection hydrate inhibitors. In this study, four derivatives were prepared by introducing hydroxypropyl-3-trimethylamine and N-2-hydroxypropyl-3-isooctyl ether groups into chitosan and carboxymethyl chitosan combined with our previous work, and their hydrate inhibition effects were further tested. By analyzing the relationship between the structural characteristics and the hydrate inhibition performance of chitosan derivatives, their hydrate inhibition mechanism was further given. The results will contribute to the research and development of green hydrate inhibitors and point out the direction for the application of chitosan and carboxymethyl chitosan derivatives as hydrate inhibitors in the future.

2. Experimental Section

2.1. Materials

Analytical grade methane with the high purity of 99.99% was purchased from Deyang Gas Co., Ltd., Jinan, China. High density chitosan (deacetylation degree (DD): 97.3%; molecular weight: $1.6 \times 10^5$) and carboxymethyl chitosan (DD: 93.2%; molecular weight: $1.7 \times 10^5$) were purchased from Shanghai McLean Biochemical Co., Ltd., Shanghai, China. Ionic liquid 1-allyl-3-methylimidazolium chloride (AmimCl, epoxy value: 65.83%) as medium for the synthesis of modified chitosan was prepared by Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences. In addition, butyl glycidyl ether (BGE), 2-Ethylhexyl glycidyl ether (EGE), and 2,3-epoxypropyltrimethylammonium chloride (EP-TAC) were all provided by Shanghai McLean Reagent Co., Ltd., Shanghai, China. Deionized water was prepared in the laboratory. Anhydrous ethanol and propanol were supplied by Tianjin Fuyu Fine Chemical Co., Ltd., Tianjin, China.

2.2. Apparatus

The diagram of the experimental setup for the methane hydrate formation is shown in Figure 1. The main parts of the device include an air inlet system, a low temperature glycol/water bath system, a reaction system and a data acquisition system. Stainless steel blind cell (effective working volume: 250 mL, maximum pressure: 25 MPa) was used to store and cool down the methane gas, and transparent sapphire cell (effective working volume: 100 mL, maximum pressure: 10 MPa) with a blade agitator was used as a reaction
cell. The pressure sensor and secondary platinum resistance thermometer (type: pt-100) were used to measure the pressure and temperature in the reactor with uncertainties of ±0.01 MPa and ±0.1 K, respectively. A data acquisition system was employed to collect the temperature and pressure.

2.3. Experimental Process

2.3.1. Preparation of Chitosan Derivatives

Four chitosan/carboxymethyl chitosan derivatives were prepared in AmimCl. Then, 0.3 g of carboxymethyl chitosan and 10 g of ionic liquid were heated to 80 °C in a 100 mL three-necked flask and stirred continuously for 4 h. Then, a certain amount of BGE was added into the three-necked flask. After another 4 h, the product was washed three times with ethanol/acetone solution. Finally, the product was freeze-dried and ground to obtain N-2-hydroxylpropyl-3-butyl ether-carboxymethyl chitosan (HBCC). In the same way, EGE was added instead of BGE and reacted for 6 h to obtain N-2-hydroxypropyl-3-(2-ethylhexyl glycidyl ether)-carboxymethyl chitosan (H2ECC) [33].

Chitosan (CS) and AmimCl with the ratio of 0.1:5 (m/m) were added to a three-necked flask placed in an oil bath at 80 °C for 4 h, and then EPTAC was added to continue the reaction for 8 h. The product was washed three times after cooling. Then, N-2-hydroxypropyl-3-trimethylammonium chloride chitosan (HTCC) was synthesized. Carboxymethyl chitosan (CMCS) and AmimCl with the ratio of 0.4:20 (m/m) were used to synthesize the N-2-Hydroxypropyl-3-trimethylamine-carboxymethyl chitosan (HTCMCh) under the same reaction conditions as HTCC.

2.3.2. Characterization of Chitosan Derivatives

Fourier-infrared (FT-IR) spectroscopy of chitosan derivatives powder was measured by Attenuated Total Reflection (ATR) method with resolution 4 cm\(^{-1}\) from 4000 cm\(^{-1}\) to 500 cm\(^{-1}\) on a Fourier-infrared spectrometer (with diamond crystal material). The type of instrument used was Nicolet FTIR-IS50.

2.3.3. Methane Hydrate Formation Experiments

Methane hydrate was produced in the apparatus shown in Figure 4. The transparent sapphire cell was cleaned three times with absolute ethanol and deionized water, and the moisture on the inner wall of the cell was removed by nitrogen flow. After tightening the cell lid, low-pressure methane (0.1 MPa) was continuously purged for 5–6 min to remove the influence of air on the experiment. Next, 30 mL of pure water or 0.1 wt% inhibitor aqueous solution was poured into the sapphire cell slowly. The valve of the sapphire cell was closed, and the blind cell was filled with 13 MPa methane gas. The stirrer (400 rpm) and cooling circulation system started working, and the ethylene glycol bath was adjusted so that the temperature in the reactor was maintained at 1 °C. After 30 min (the temperature of the reaction cell remains unchanged, and the pressure in the blind cell is stable), 6 MPa methane gas is charged into the reaction cell, and the reaction is continued until equilibrium. The remaining gas was discharged outside through an outlet “vent” at the end of the reaction. Figure 5 showed the flow chart of the experimental operation. Each system of experiment was repeated three times to ensure the accuracy of the results.
Figure 4. Schematic of the experimental apparatus used for hydrate formation. DPT: differential pressure transducer; RTD: resistance thermocouple detector; DAS: data acquisition system; V1, V2 and V3: valves.

Figure 5. The operation flow chart of the methane hydrate formation experiments.

3. Results

3.1. Characterization of Chitosan Derivatives

It can be seen in the FT-IR spectrum of chitosan derivatives (Figure 6), 1648 cm\(^{-1}\), 2952 cm\(^{-1}\), 1620 cm\(^{-1}\) and 1418 cm\(^{-1}\) represent secondary amine -N-H, carbocyclic -C-H vibrational peaks, -C = O and -C-H vibrational peaks in CMCS, respectively. We found that 2920 cm\(^{-1}\) and 2848 cm\(^{-1}\) are the peaks of -CH\(_2\) and -CH\(_3\) groups in HBCC or H2ECC substituents, respectively. We also found that 1620 cm\(^{-1}\) is a red-shifted -N-H vibrational peak, and that 3433 cm\(^{-1}\), 1595 cm\(^{-1}\), 1476 cm\(^{-1}\) and 1388 cm\(^{-1}\) represent -NH or -OH vibration peak, hydrogen bond (indicating successful grafting), methyl -CH\(_3\) vibration peak and secondary on substituent amine -NH vibration peak, respectively. In the FT-IR spectra of CS and HTCC, the peaks at 1660 cm\(^{-1}\), 1595 cm\(^{-1}\) and 1475 cm\(^{-1}\) are the vibration peaks...
of primary amine, the methyl vibration peak of quaternary amine -N-CH₃ and adjacent -CH vibrational peaks on aliphatic chains linked by tertiary amines, respectively. The peaks at 2370 cm⁻¹ and 2800–3000 cm⁻¹ are the -CH stretching vibration peaks of methyl group. The bending vibration peaks of methyl group and the -NH bending vibration peaks of amino groups appear at 1400 cm⁻¹ and 1560 cm⁻¹, respectively. With the increase in the aliphatic chain length, the stretching vibration peak of methylene group appears at 1081 cm⁻¹. Infrared spectral data proved that the grafting of chitosan derivatives was successful [34,35]. The molecular structure of chitosan/carboxymethyl chitosan derivatives is shown in Table 1.

![Figure 6. FT-IR spectra of chitosan derivatives.](image)

**Table 1.** Molecular structures of various chitosan derivatives.

| Name                                      | Structure          | Name                                      | Structure          |
|-------------------------------------------|--------------------|-------------------------------------------|--------------------|
| Chitosan (CS)                             | ![Structure](image) | Carboxymethyl chitosan (CMCS)             | ![Structure](image) |
| N-2-hydroxypropyl-3-trimethylamine chitosan (HTCC) | ![Structure](image) | N-2-hydroxypropyl-3-isooctyl ether-O-carboxymethyl chitosan (H2ECC) | ![Structure](image) |
| N-2-hydroxypropyl-3-trimethylamine-O-carboxymethyl chitosan (HTCMCh) | ![Structure](image) | N-2-hydroxypropyl-3-butyl ether-O-carboxymethyl chitosan (HBCC) | ![Structure](image) |

3.2. Methane Hydrate Formation Experiments

Figure 7 showed the typical temperature and pressure curves of methane hydrate formation at 6 MPa and 1 °C in pure water system. From the figure, we could clearly see that there was a slight downward trend in pressure in the first 14 min after the reaction.
started. This was because a small amount of methane dissolved in water under the function of stirring after the gas entered the reactor. After that, the pressure was basically maintained at a stable plateau, which was called the induction period of hydrate formation, and started to change after 157 min. During this period, a small amount of hydrate nuclei was formed. Under the action of the crystal nucleus, the hydrate began to grow slowly and the pressure dropped slowly. After about 500 min, the pressure dropped sharply due to the formation of a large number of hydrate particles in the previous stage. In the stage of rapid pressure drop, the low temperature environment of the system was destroyed, and the temperature rose rapidly to about 3.5 °C. When the reaction reached equilibrium, the pressure no longer changed and the temperature returned to the initial temperature of the reaction [36]. The hydrate formation process consumed 0.073 mol methane gas, and the calculation formula was as follows [37]:

\[ n = \frac{P_0 V}{Z_0 RT_0} - \frac{P V}{Z RT} \]  

(1)

where \( P_0 \) and \( P \) were the initial and equilibrium pressures of the reactor, respectively. \( V \) was the volume of the reactor. \( Z_0 \) and \( Z \) were the compressibility factors of the system in the initial and equilibrium state, respectively. \( R \) was the universal gas constant.

Figure 7. Typical temperature/pressure–time curve of methane hydrate formation process.

Figure 8 showed a typical methane hydrate formation process photographs in a pure water system. It could be seen from the photos taken by the Sony α6000 camera that the formation of methane hydrate was not found at the beginning of the reaction. A few hydrate particles appeared after a period of time (hydrate induction time). When \( t = 156.2 \) min, the small volume of methane hydrate that was distributed in the solution came to light in the red box. Under the action of stirring, the gas–liquid interface became larger. The gas was dissolved in the water phase continuously and formed hydrate cages with water molecules rapidly. Therefore, hydrates were preferentially formed near metal stirrers. When \( t = 157 \) min, more uniformly distributed small particles of methane hydrate appeared in the solution, and the hydrates block near the stirrer enlarged significantly. When \( t = 159 \) min, the small particles of hydrate in the solution had completely blocked the view [38]. It was consistent with the hydrate formation process revealed in Figure 7.
In this experiment, chitosan derivatives, which had been prepared, were used as methane hydrate inhibitors, and their inhibition effects were studied. The optimized pressure change curves of each system containing hydrate inhibitors in the experimental process are shown in Figure 9. Each group of experiments reached a balance at the end time of the curve. Standard induction time methods were used to evaluate its effect as hydrate inhibition.

![Figure 8](image-url)  
**Figure 8.** Typical hydrate formation process under 6 MPa and 1 °C in the pure water system.

It could be clearly seen from Figure 9, except for CMCS, other inhibitors could prolong the induction period of hydrate formation to a certain extent. The average induction time of methane hydrates in different systems was shown in Table 2. The induction time of hydrate in the CS inhibitor system had the highest values (20.38 h), which was 17.58 h (7.28-fold) higher than the induction time of the pure water system. In the research of Saberi, under the conditions of 8 MPa, 4 °C and 500 rpm, the induction time of 2 wt% PVP was 126.5 min, which was only 2.69-fold longer than the induction time of hydrate formation in the pure water system [39]. Idress had studied the inhibitory effect of disaccharide, carboxymethylcellulose and stevia rebaudiana on methane hydrate, and found that the inhibitory effect of disaccharide was the best, but it only prolonged the induction time by 1.1-fold compared with the blank experiment [40].

![Figure 9](image-url)  
**Figure 9.** Variation in pressure with time in different inhibitor systems.

| Inhibitor | Average Induction Time (h) | Growth Time (h) |
|-----------|-----------------------------|-----------------|
| water     | 4.14                        | 9.90            |
| CS        | 2.80                        | 23.67           |
| CMCS      | 2.07                        | 23.67           |
| HTCC      | 5.90                        | 16.53           |
| HTCMCh    | 7.70                        | 19.12           |
| HBCC      | 3.03                        | 7.70            |
| H2ECC     | 2.96                        | 19.12           |
| H3ECC     | 2.98                        | 23.67           |

| System    | Pressure (MPa) | Time (min) | Hydrate Growth |
|-----------|----------------|------------|----------------|
| water     | 6.0            | 2500       | 6.0            |
| CS        | 5.0            | 2500       | 5.0            |
| CMCS      | 4.0            | 2500       | 4.0            |
| HTCC      | 3.0            | 2500       | 3.0            |
| HTCMCh    | 2.0            | 2500       | 2.0            |
| HBCC      | 1.0            | 2500       | 1.0            |
| H2ECC     | 0.0            | 2500       | 0.0            |
| H3ECC     | 0.0            | 2500       | 0.0            |

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![Figure 9](image-url)  
**Figure 9.** Variation in pressure with time in different inhibitor systems.
Table 2. The average induction time of hydrates formation in the methane–water systems with 0.1 wt% chitosan derivatives at 1 °C, 6 MPa and 400 rpm.

| Additives | $P_E$ (MPa) | Average Induction Time (h) | Growth Time (h) |
|-----------|-------------|----------------------------|-----------------|
| water     | 4.14        | 2.80                       | 9.90            |
| CS        | 2.98        | 20.38                      | 15.38           |
| HTCC      | 2.96        | 5.90                       | 16.53           |
| CMCS      | 2.98        | 2.07                       | 23.67           |
| HTCMCh    | 3.03        | 7.70                       | 19.12           |
| HBCC      | 3.47        | 3.42                       | 11.17           |
| H2ECC     | 2.96        | 3.97                       | 21.52           |

Additives: Hydrate inhibitors; $P_E$: Reaction equilibrium pressure.

Obviously, the inhibition hydrate effect of 0.1 wt% CS in the experiment was better than commercial inhibitors and some natural hydrate inhibitors. The inhibition effect and potential value of CS as a dynamic hydrate inhibitor were verified. The inhibitory effects of other chitosan derivatives were ranked as follows: HTCMCh > HTCC > H2ECC > HBCC. Observing the molecular structure of the derivatives in Table 1, it can be seen that the number of methyl groups (-CH$_3$) had a greater influence on the molecular inhibition effect than the length of the alkyl chain. Carboxymethyl chitosan could not inhibit the formation of hydrate, only promote it. However, the addition of trimethyl quaternary ammonium group -N(-CH$_3$)$_3$ and alkyl ether -O-(CH$_2$)$_n$-CH$_3$ improved the inhibitory effect of carboxymethyl chitosan, and a better inhibitor than carboxymethyl chitosan was obtained.

Figure 10 showed the general trend of methane gas consumption in various systems. Methane gas consumption was positively correlated with pressure changes. The end of the curve was the time when the reaction has just reached equilibrium. CMCS, H2ECC, HTCMCh, HTCC and CS exhibited the same total gas consumption. The consumption of methane in the dissolution phase was not discussed in this experiment. During the induction phase of methane hydrate formation, gas consumption was low because gas was only available for hydrate nucleation. During the hydrate induction period, the consumption of methane gas was very small. After the hydrate induction period, the consumption rate of methane increased greatly due to the rapid formation of hydrate. Figure 11 visually showed the amount of methane gas (mol) consumed by different systems when they reached equilibrium. Combined with Figure 10 and Table 2, although chitosan and its derivatives could obviously prolong the induction time of methane hydrate formation, they had certain shortcomings in gas consumption. For the system with pure aqueous solution, the gas consumption is 0.073 mole in equilibrium. However, the addition of chitosan and its derivatives increased the amount of methane consumption to about 0.11 mole in equilibrium.

Figure 10. Total gas consumption curves of various systems.
Then, the time required for gas consumption to reach 0.073 mol in each system was summarized in Table 3. From Table 3, it could be seen that the pure water system consumed 0.073 mole methane gas at 760 min. However, CMCS and HBCC significantly increased the rate of methane consumption and reduced the time to 690 min and 648 min, respectively. For other inhibitors that could significantly prolong hydrate induction time, the gas consumption rate was also significantly slowed down. Among them, chitosan could prolong the hydrate inhibition time from 760 to 1766 min, which again verified its excellent hydrate inhibition performance from the perspective of gas consumption. Moreover, the modification of CS and CMCS by trimethyl quaternary ammonium salt group (i.e., HTCC and HTCMCh) also significantly slowed down the rate of gas consumption and prolonged the time to 1496 and 1410 min.

Table 3. The time required for gas consumption to reach 0.073 mol in each system.

| System    | Water | CS  | CMCS | HTCC | HTCMCh | HBCC | H2ECC |
|-----------|-------|-----|------|------|--------|------|-------|
| \( t_{0.073 \text{ mol}} \) (min) | 760   | 1766| 690  | 1496 | 1410   | 648  | 1098  |

3.3. Mechanism of Methane Hydrate Inhibition

It was known that chitosan had high hydrophobicity, while carboxymethyl chitosan showed strong hydrophilicity. Therefore, when chitosan was added to the aqueous solution, it was mainly distributed at the gas–liquid interface, which effectively prevented methane molecules from entering the water solution and reduced the driving force of methane hydrates, as shown in Figure 12a. Finally, the induction time of hydrate formation was significantly prolonged by chitosan. When the trimethyl quaternary amide group was introduced into chitosan (i.e., HTCC), the hydrophobicity of chitosan was significantly reduced, which would further weaken the gas–liquid interface’s hindrance to methane gas dissolution process, and was not conducive to the inhibition of hydrates.
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Although the hydrophilic carboxymethyl chitosan could not inhibit the nucleation of hydrates, it could significantly inhibit the growth of hydrates, which could be verified by Table 2, i.e., CMCS extended the growth time of hydrates in the pure water system from 9.9 to 23.67 h. CMCS molecules in the water phase could adsorb on the surface of hydrate cages and form intermolecular hydrogen bonds (H-bonds), which hindered the subsequent growth of methane hydrates, as shown in Figure 12b. The addition of trimethyl quaternary ammonium group -N(-CH₃)₃ and alkyl ether -O-(CH₂)n-CH₃ into CMCS (i.e., HTCMCh, H₂ECC and HBCC) improved the hydrophobicity as well as prolonged the hydrate induction time. At the same time, the introduction of trimethyl quaternary ammonium group increased the ion content in the aqueous solution, which further inhibited the nucleation and growth of methane hydrates.

4. Conclusions

The inhibitory properties of chitosan/carboxymethyl chitosan and their four derivatives on methane hydrate were tested at 6 MPa, 1 °C and 400 rpm. The experimental results showed that the hydrophobic performance of the additives was positively correlated with the methane hydrate inhibition performance. Chitosan with strong hydrophobicity showed the best inhibition performance of methane hydrate and could prolong the hydrate induction time from 2.8 to 20.38 h. It was found that chitosan could effectively prevent methane gas from entering the water solution and reduced the driving force of methane hydrates, resulting in the extension of hydrate induction time.

The number of methyl groups had a more significant effect on the inhibitory effect than the chain length of the alkyl groups. The hydrate inhibition effect of CMCS was the worst, but could be improved by the introduction of hydroxypropyl-3-trimethylamine and N-2-hydroxypropyl-3-isooctyl ether groups based on the enhancement of the molecular hydrophobicity. At the same time, the introduction of trimethyl quaternary ammonium group

![Figure 12. Inhibitory mechanism of methane hydrate formation under the action of hydrophobic additives: (a) Inhibitor with strongly hydrophobicity; (b) Inhibitor with weakly hydrophobicity.](image-url)
increased the ion content in the aqueous solution, which further inhibited the nucleation and growth of methane hydrates. This work is supposed to serve as an inspiration for the development and modification of green kinetic hydrate inhibitors in the future. The developed hydrate inhibitors in this work will help to ensure the slow assurance safety of natural gas transportation in the pipeline.

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