

A Novel Atmospheric-Pressure, Low-Temperature Evaluation Method for Natural Gas Hydrate Dissociation Inhibitors Utilizing Cyclopentane Hydrate[#]

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ABSTRACT

During natural gas hydrate (NGH) drilling and production, changes in reservoir temperature and pressure conditions, along with heat generated by drilling operations, can lead to partial or even uncontrolled hydrate dissociation. This phenomenon increases the risk of wellbore instability and jeopardizes drilling efficiency and safety. Hydrate dissociation inhibitors have thus emerged as critical components for stabilizing hydrate-bearing formations and mitigating drilling risks, thereby supporting efficient NGH extraction. However, current evaluation methods for NGH inhibitors predominantly focus on inhibiting hydrate formation, with relatively limited research addressing performance assessment of dissociation inhibitors. Based on a comprehensive literature review, this study first demonstrates the feasibility of using cyclopentane hydrate as a substitute for methane hydrate in evaluating dissociation inhibitor performance. An experimental protocol was designed accordingly to assess inhibitor efficacy using cyclopentane hydrate. Under this constructed evaluation framework, the equilibrium temperature of cyclopentane hydrate was measured at 6.73°C, and 0.7% lecithin solution effectively delayed dissociation for 53 minutes. These results validate the practicality and reliability of the proposed assessment methodology.

Keywords: cyclopentane hydrate, dissociation inhibitor, inhibitor evaluation, lecithin

1. INTRODUCTION

Direct sampling and field experiments in gas hydrate reservoirs are challenging due to significant technical difficulties and high costs, making laboratory-based simulation the primary approach for in-depth investigation. To facilitate efficient and convenient

research on gas hydrate formation and inhibition, existing experimental setups have been integrated and technologically upgraded. Simulation apparatuses for hydrate formation, dissociation, and inhibition essentially provide high-pressure and low-temperature reaction environments. However, since the primary components of natural gas exhibit low solubility in water, hydrate formation in static pure water systems typically initiates at the gas-liquid interface—where the gas concentration gradient is highest—forming a thin film that impedes further contact between gas and water, leading to exceedingly slow formation kinetics [1]. This slow nucleation not results in low formation rates but also leads to suboptimal gas storage efficiency, often failing to meet theoretical expectations and industrial application standards [2].

The evolution of wellbore simulation devices for thermal and phase behavior has progressed from non-visualized reactors to sapphire visual stirred reactors, which address the inability to directly observe hydrate formation. Despite their transparency and pressure resistance, existing single-chamber sapphire reactors do not support parallel comparative experiments and lack multi-zone programmable temperature control. Wang et al. [3] developed a dual-reactor visual apparatus for wellbore hydrate formation, inhibition, and dissociation, overcoming these limitations. While various methods exist for evaluating hydrate inhibitors—such as high-pressure autoclaves, viscosity measurements, laser-based techniques, rocking cells, and flow loops—most operate under high-pressure conditions, introducing significant experimental risks and operational complexity. Abojaladi N et al. [4] demonstrated consistent performance of several common anti-agglomerants in both pressurized methane hydrate and atmospheric cyclopentane hydrate systems. Similarly, Ren et al. [5] employed cyclopentane hydrates for

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preliminary screening of amino acid-based promoters and validated three inhibitors under high-pressure methane conditions, confirming results from the cyclopentane system [6]. Ho Van Son et al. [7] measured and simulated phase equilibrium data of cyclopentane hydrate in pure water and saline solution, reporting an equilibrium temperature of 7.1°C in pure water.

In this study, we establish a method for evaluating hydrate dissociation inhibitors using cyclopentane hydrate as a substitute for methane hydrate under low-temperature and atmospheric-pressure conditions, significantly accelerating the initial screening of effective inhibitors during early-stage development.

2. EXPERIMENTAL AND METHOD

cold field emission scanning electron microscope (Hitachi).

2.2 Synthesis of cyclopentane hydrate

The experimental procedure was conducted using two flasks, each containing an appropriate amount of cyclopentane. Ice particles were introduced into the cyclopentane in both flasks. One flask was subjected to mechanical stirring, while the other remained unstirred. The temperature of the ice-water bath was gradually elevated to 3.2 °C and maintained under cooling until the reaction proceeded to completion.

2.3 Cyclopentane hydrate evaluation hydrate inhibitor effect experiment

2.3.1 Design and assembly of experimental instrument

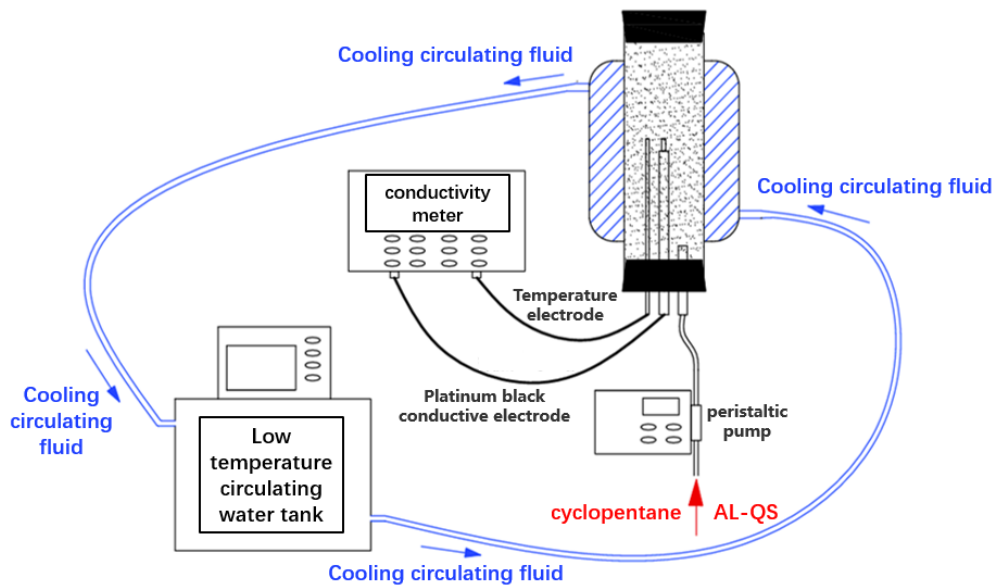


Fig. 1 Experimental device diagram of cyclopentane hydrate formation, decomposition and inhibition

2.1 Materials and Experimental apparatus

Materials used in this study included cyclopentane (96% purity, Beijing InnoChem Technology Co., Ltd.), quartz sand (analytically pure, Shanghai Macklin Biochemical Technology Co., Ltd.), anhydrous ethanol (99% purity, Shanghai Energy Chemical Chemical Co., Ltd.), and lecithin (98% purity, Beijing Huawei Ruike Chemical Co., Ltd.).

Key instruments employed were a KX-DW-101 low-temperature circulating water bath (Jiangsu Jintan Kexi Instrument Co., Ltd.), a BS100-1A/WX10-14 peristaltic pump (Baoding Qili Constant Current Pump Co., Ltd.), a straight cooling reactor (Beijing Haiboxing Technology Co., Ltd.), a DDSJ-308F conductivity meter (Shanghai Yidian Scientific Instrument Co., Ltd.), and an SU8020

Leveraging the physical properties of cyclopentane—namely its lower density than and immiscibility with water—along with its capacity to form structure-II cyclopentane hydrate under low-temperature and atmospheric-pressure conditions, we designed and integrated a suite of specialized experimental apparatus. A conventional straight condenser tube was modified by enlarging the internal diameter of the inner tube and shortening the non-cooled sections at both ends to create a suitable reaction vessel. In accordance with the comprehensive evaluation framework for natural gas hydrate dissociation inhibitors proposed by Wang et al. [8], a conductivity meter was employed to quantitatively monitor the formation and dissociation of cyclopentane hydrate within a mixture of cyclopentane, quartz sand, water, and ice particles. A perforated rubber stopper was fitted at the bottom of the vessel to maintain sealing

while accommodating a platinum-black conductivity electrode, temperature probe, and fluid injection line. Systematic tests with quartz sand of varying particle sizes (20-40, 40-60, 60-80, 80-120, 120-200, and 200-220 mesh) revealed that 40-60 mesh sand provided optimal performance, ensuring data accuracy, visual clarity, and suitable pore structure for both hydrate formation and inhibitor infiltration. A low-flow peristaltic pump was used to inject cyclopentane and inhibitor solutions upward from the bottom, facilitating slow and uniform saturation of the interstitial spaces between the sand and hydrate; this bottom-up approach also displaced unreacted cyclopentane and ensured thorough contact between the inhibitor and the hydrate surface. Anhydrous ethanol was circulated as a coolant to achieve temperatures of -16°C or lower within the reaction mixture, providing the necessary supercooling conditions for cyclopentane hydrate formation. The fully assembled experimental setup is schematically illustrated in Fig. 1.

2.3.2 Experiment on formation and decomposition characteristics of cyclopentane hydrate



Fig. 2 40-60 mesh quartz sand mixed with ice particles

Prior to initiating the experiment, a mixture of 40–60 mesh quartz sand and deionized water ice particles at a mass ratio of 5:1 was thoroughly blended (Fig. 2) and stored together with cyclopentane at -20°C for pre-cooling. Following full assembly of the experimental setup, the straight cooling reactor was verified for air tightness, with proper electrical connections established for the conductivity meter and peristaltic pump, and normal operation confirmed for both the platinum-black conductivity electrode and temperature sensor. After the quartz sand located outside the refrigerated zone of the reactor had fully absorbed water and reached saturation, excess deionized water was removed using the peristaltic pump.

With these preparatory steps completed, the experiment for cyclopentane hydrate formation and dissociation commenced: the low-temperature

circulating bath was powered on to circulate coolant at -16°C , providing the necessary supercooling conditions for hydrate formation; the conductivity meter was activated to monitor temperature and conductivity data collected via the corresponding electrodes; when the internal temperature decreased to -10°C , the mixture of 40–60 mesh quartz sand and deionized water ice particles was loaded into the reactor and compacted to simulate a porous sandstone reservoir environment; after temperature stabilization, pre-chilled cyclopentane (-20°C) was delivered into the reactor using the peristaltic pump until the liquid level exceeded that of the sand–ice mixture; the conductivity measurement function was initiated with a total of 480 data points acquired at 60-second intervals; the coolant temperature was then adjusted to 3.2°C to induce rapid cyclopentane hydrate formation, which was sustained for 3 hours; upon complete hydrate formation, pre-cooled hydrate dissociation inhibitor solution was injected via the peristaltic pump, displacing the insoluble cyclopentane from the simulated reservoir pores and allowing the inhibitor to saturate the pore space—the system was subsequently held static for 30 minutes to ensure sufficient interaction between the inhibitor and hydrate surfaces; finally, the coolant temperature was raised to 7.8°C and maintained until the conductivity meter had completed recording all time-dependent conductivity and temperature measurements.

3. RESULTS AND DISCUSSION

3.1 Formation of cyclopentane hydrate

temperature to 10 °C and maintaining static conditions for 2 minutes led to the mixture shown in (e), where

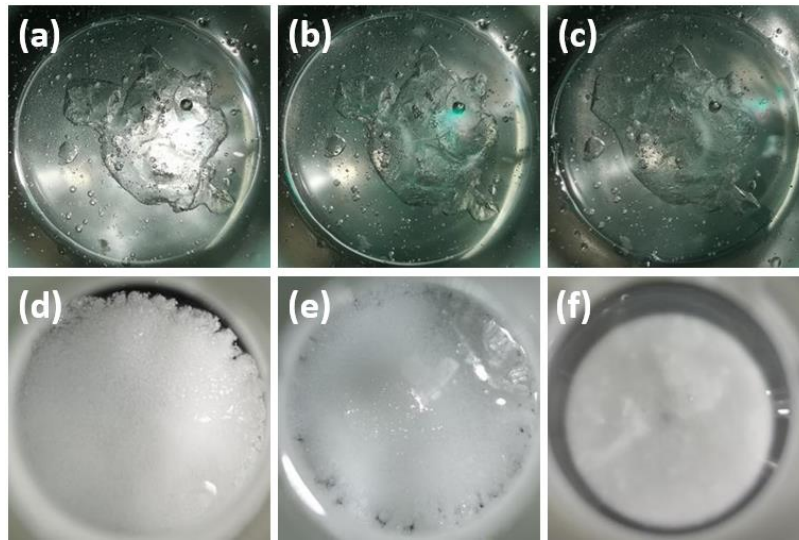


Fig. 3 Cyclopentane hydrate formed at low temperature and atmospheric pressure

The experimental product, as shown in Figure 3, was successfully synthesized under laboratory conditions. Panels (a), (b), and (c) depict hydrate formation experiments conducted in an ice-water bath maintained at -3 °C. Over time, crystalline cyclopentane hydrate was observed to form exclusively at the interface between cyclopentane and water; however, crystal growth ceased after a certain period, resulting in a stable hydrate layer confined to the liquid-liquid interface. In contrast, the formation process illustrated in panels (b), (e), and (f) was carried out under identical subzero temperature and duration but with mechanical stirring at 600 rpm, yielding uniformly dispersed cyclopentane hydrate particles as seen in (b). Subsequently, raising the bath

partial dissociation and aggregation of hydrate particles into larger clusters occurred. Further maintenance at 10 °C ultimately resulted in nearly complete dissociation and re-stratification into distinct cyclopentane and water phases, as visualized in (f). These observations confirm that cyclopentane hydrate formation, dissociation, and inhibition can be effectively simulated under atmospheric pressure and low-temperature conditions using mechanical agitation and controlled cooling.

3.2 Experiment on formation and decomposition characteristics of cyclopentane hydrate

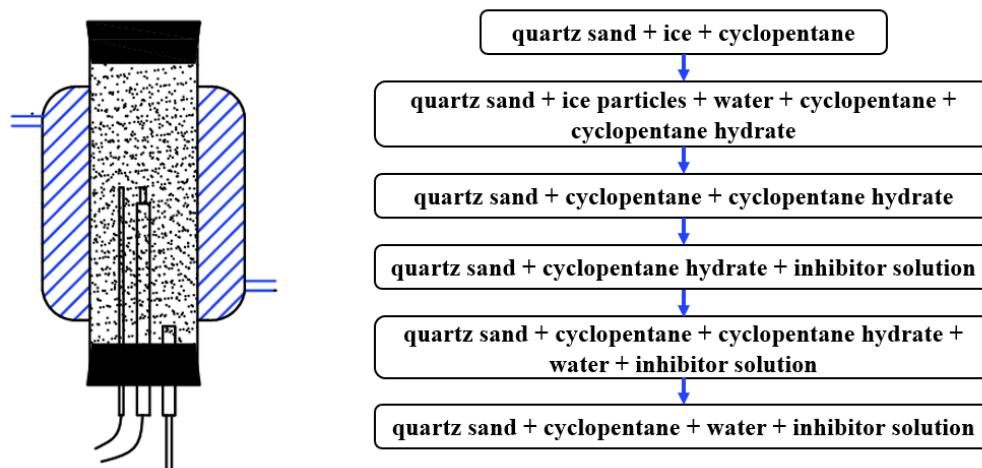


Fig. 4 Phase change of mixture composition in reaction vessel

3.2.1 Experimental principles

By monitoring the changes in electrical conductivity near the measurement points within the reaction vessel, we were able to analyze the specific phase of cyclopentane hydrate formation or dissociation. Initially, the vessel contained a mixture of quartz sand, ice particles, and cyclopentane. When the temperature of the low-temperature circulating bath was raised above 0°C, the ice particles gradually melted, enabling contact with cyclopentane and subsequent formation of cyclopentane hydrate at the interface, resulting in a multi-phase system comprising quartz sand, ice, water, cyclopentane, and cyclopentane hydrate. Due to the presence of excess cyclopentane, the mixture evolved into a state of quartz sand, cyclopentane, and cyclopentane hydrate after complete melting of ice and full hydrate conversion. As the experiment progressed, pre-cooled hydrate dissociation inhibitor solution was introduced via a peristaltic pump, displacing the unreacted cyclopentane and transforming the system into a composition of quartz sand, cyclopentane hydrate, and inhibitor solution. Upon increasing the bath temperature to 7.8°C, which exceeds the equilibrium temperature of cyclopentane hydrate, dissociation commenced, yielding a mixture of quartz sand, cyclopentane, hydrate, water, and inhibitor. Ultimately, complete dissociation of the hydrate resulted in a final composition of quartz sand, cyclopentane, water, and inhibitor solution; this sequence of phase transitions is illustrated in Figure 4.

Continuous acquisition of conductivity and temperature data near the measurement points throughout these stages allowed the construction of characteristic curves for hydrate formation and dissociation. Analysis of the trend in these curves enabled precise identification of the timing of key events: the onset and completion of hydrate formation, as well as the initiation and conclusion of dissociation. The point at which the local temperature recorded by the platinum-black conductivity electrode reached the equilibrium temperature of cyclopentane hydrate was designated as the reference start point for evaluating the effectiveness of the dissociation inhibitor. The corresponding end point was determined based on the inflection in the conductivity curve—specifically, the moment when the slope turned from positive to negative or exhibited a sudden increase. The duration between these two points was defined as the effective time period over which the inhibitor delayed the dissociation of cyclopentane hydrate.

3.2.2 Equilibrium temperature of cyclopentane hydrate

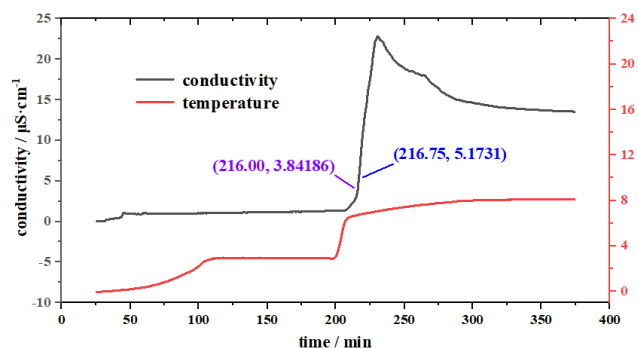


Fig. 5 Characteristics of cyclopentane hydrate formation and decomposition

The experimental results yielded characteristic curves of cyclopentane hydrate formation and dissociation, as shown in Fig. 5. Analysis of conductivity and temperature variations revealed that complete hydrate formation was achieved prior to the introduction of the dissociation inhibitor at the 200-minute mark. The hydrate remained stable during a subsequent rapid temperature increase that remained below its equilibrium temperature. A sharp increase in the slope of the conductivity–time curve occurred between 216 and 216.75 minutes, as the temperature gradually rose to 6.73 °C, indicating the onset of hydrate dissociation. Based on comprehensive analysis of the experimental

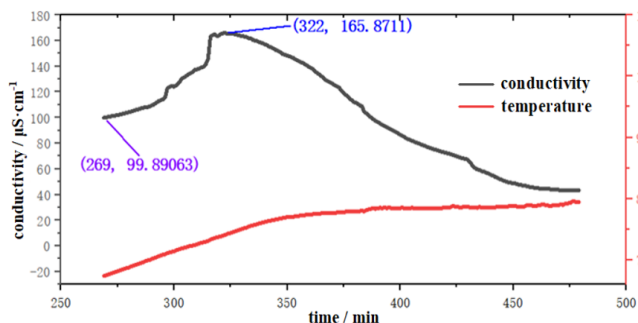


Fig. 6 Cyclopentane hydrate decomposition curve inhibited by 0.7% lecithin solution

data and dissociation characteristics, the equilibrium temperature of cyclopentane hydrate under this evaluation system was determined to be 6.73 °C. This dataset served as a blank control (no inhibitor added) for assessing the performance of synthesized dissociation inhibitors in delaying hydrate decomposition.

To validate the proposed method for evaluating inhibitor efficacy, a 0.7% lecithin solution—selected based on prior studies concerning the concentration-dependent inhibition effect of lecithin—was tested [9].

The resulting conductivity and temperature evolution curves (Fig. 6) indicated a gradual slope

increase beginning at 269 minutes due to temperature influence, with the slope turning from positive to negative at 322 minutes, marking the point at which dissociation commenced under inhibition. Thus, the effective inhibition duration provided by 0.7% lecithin solution was determined to be 53 minutes, from minute 269 to 322.

4. CONCLUSIONS

Based on an extensive literature review, this study summarizes the evolution of simulation and evaluation systems for the formation, dissociation, and inhibition of natural gas hydrates, and outlines the advantages and limitations of using natural gas hydrate systems for evaluating the performance of dissociation inhibitors. Building upon theoretical and experimental support from previous work advocating cyclopentane hydrate as a substitute for methane hydrate in preliminary inhibitor screening, we established a novel evaluation methodology for assessing hydrate dissociation inhibitors and conducted a feasibility analysis. Application of this method yielded characteristic curves of cyclopentane hydrate formation and dissociation, from which an equilibrium temperature of 6.73°C was determined under the specified experimental conditions. These baseline curves, obtained in the absence of inhibitors, served as a reference for evaluating the performance of dissociation inhibitors. Subsequently, the system was used to test a 0.7% lecithin solution, which effectively delayed cyclopentane hydrate dissociation for a total duration of 53 minutes. The established evaluation methodology not only provides an efficient screening tool for laboratory research but also outlines a clear technical pathway for field application of dissociation inhibitors. Future work will focus on pilot-scale validation of high-performance inhibitors identified through this system and developing tailored injection strategies for specific hydrate-bearing formations to ultimately enhance drilling safety and gas production efficiency in real-world NGH development projects.

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