



Dual inhibition effects of diamines on the formation of methane gas hydrate and their significance for natural gas production and transportation



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ABSTRACT

Dual (thermodynamic and kinetic) inhibition effects of piperazine (PZ) and hydrazine (HZ), two representative diamines, on the formation of CH₄ hydrate were investigated, primarily focusing on thermodynamic, spectroscopic, and computational analyses for their potential application in natural gas production and transportation. The phase behavior demonstrated that the addition of PZ and HZ shifts the CH₄ hydrate equilibrium lines to higher pressure or lower temperature regions depending on diamine concentrations. The ¹³C NMR and Raman spectra of the CH₄ + diamine hydrates revealed that PZ and HZ are not enclathrated in the cages of CH₄ hydrate and do not affect the hydrate structure. The time-dependent growth patterns and the induction time of CH₄ hydrate in the presence of diamines were observed via in-situ Raman spectroscopy. HZ showed a more significant thermodynamic inhibition effect, slower hydrate growth, and longer induction time than PZ did. Interaction energy calculation using density functional theory (DFT) indicated that diamine molecules could disrupt the hydrogen bonding networks of hydrate cages, leading to destabilization of gas hydrate and retardation of hydrate nucleation and growth. Experimental and computational results demonstrated that both PZ and HZ can function as both kinetic and thermodynamic hydrate inhibitors for CH₄ hydrate.

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1. Introduction

Clathrate hydrates or gas hydrates are non-stoichiometric crystalline compounds composed of water cages (host) and gas molecules (guest). These ice-like solid compounds have a van der Waals interaction between host water molecules and entrapped gas molecules under high pressure and low temperature conditions. Naturally occurring clathrate hydrates are called natural gas hydrates (NGHs), which are mainly found in the permafrost of the Arctic regions and the deep ocean sediments of continental margins [1,2]. Since an enormous amount of methane gas is enclosed in the deposited NGHs, NGHs are considered a promising future energy source, and thus, national programs in several countries have been conducted for the research and production of NGHs [1,3]. Moreover, gas hydrates can be utilized in the various fields such as natural gas storage and transportation, carbon dioxide capture and storage (CCS), and desalination [4–9]. However, despite these advantageous applications, there has been an industrial concern about gas hydrates in gas and oil industries. Specifically,

in the process of production and transportation of natural gas and oil, some hydrocarbons come into contact with water throughout the pipelines under high pressure and low temperature conditions, leading to gas hydrate formation and subsequent pipeline blockage, which is one of the critical industrial problems in energy production. Pipeline plugging is an important issue to be solved because it is directly related to the safety concerns and financial losses in gas and oil industries [10]. Injection of hydrate inhibitors has been considered as a promising method to resolve the pipeline plugging, and these hydrate inhibitors can be divided into thermodynamic hydrate inhibitors (THIs), kinetic hydrate inhibitors (KHIs), and anti-agglomerants (AAs) [11–14].

Thermodynamic hydrate inhibitors (THIs) are used to translocate hydrate phase equilibrium lines to the thermodynamically unstable regions of gas hydrates, where temperature is lowered and pressure is elevated. On the other hand, kinetic hydrate inhibitors (KHIs) can retard hydrate nucleation and growth when used in much smaller amounts compared to THIs. Anti-agglomerants (AAs) prevent gas hydrate crystals from entering into a dense solid state and, thus, keep them in a fluidal slurry form. Currently, the injection of THIs such as methanol and ethylene glycol is being adopted as a convenient solution by many oil and gas industries to avoid

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hydrate formation [15–18]. In hydrate inhibition, the existence or strengthening of hydrogen bonds between host water molecules and inhibitor molecules is considered to be a crucial factor for shifting hydrate equilibrium lines or preventing crystal growth of gas hydrates [1]. When chemical substances containing highly electronegative atoms such as nitrogen, oxygen, and fluorine are added to the hydrate formation systems, they are able to attract hydrogen atoms of water molecules in the host hydrate cages, which results in destabilization of gas hydrate structures. Methanol and glycols are well-known THIs containing oxygen atoms that are electronegative enough to attract the hydrogen atoms of water molecules in the hydrate lattices [10,19–21]. Some compounds containing electronegative nitrogen atoms have also been examined for their inhibition effects on gas hydrate formation [22–26]. Park et al. introduced morpholine (C_4H_9NO) and ammonium fluoride (NH_3F) as new THIs, and they confirmed that morpholine is able to act as both thermodynamic and kinetic inhibitors [22,23]. Diazine isomers, which contain two nitrogen atoms, were studied for their thermodynamic inhibition effects depending on the molecular properties such as structure, size, and dipole moment [26].

Two diamines, piperazine ($C_4H_{10}N_2$, PZ) and hydrazine (N_2H_4 , HZ), were selected as potential candidates for hydrate inhibitors in this study. PZ is a cyclic amine with two nitrogen atoms, and HZ is the simplest amine having two nitrogen atoms. These diamines have been widely used in various industries as well as in CO_2 absorption processes [27–30]. Therefore, the objective of this study is to investigate the thermodynamic and kinetic inhibition effects of PZ and HZ on methane (CH_4) gas hydrate formation and thus, to find out whether they are potentially applicable for flow assurance. The first objective of this study is to observe the phase equilibrium shift of CH_4 hydrate in the presence of PZ and HZ to harsh conditions in order to identify their thermodynamic inhibition effect, and the second objective is to confirm kinetic inhibition effect of PZ and HZ on CH_4 hydrate formation by measuring and observing the induction time and growth patterns.

In this study, the hydrate phase equilibria of the CH_4 + water + diamine systems were measured to examine the thermodynamic inhibition effect of diamines. The structure of the CH_4 + PZ and CH_4 + HZ hydrates was identified using ^{13}C NMR and Raman spectroscopy to confirm the enclathration of inhibitors in the hydrate cages and the consequent structure transition. In addition, in-situ Raman spectroscopy was adopted to observe the growth patterns of each cage and the cage occupancy behavior during hydrate formation in the presence of diamines. The induction time of CH_4 hydrate formation was also measured using in-situ Raman spectroscopy to examine the kinetic inhibition effect of diamines. Furthermore, computational analysis using density functional theory (DFT) was also applied to understand the inhibition effect from the structural configuration and interaction energy.

2. Experimental

2.1. Materials and apparatuses

CH_4 gas with a purity of 99.9% was supplied by MS Gas Co. (Republic of Korea). PZ (99% purity) and HZ (35 wt% solution in water) were purchased from Sigma-Aldrich Chemical Co. (USA). Double distilled and deionized water was used in this experiment. The experimental apparatus was specially designed to accurately measure the pressure and temperature during the hydrate formation and dissociation process. The temperature and pressure profiles according to experimental time were provided in the supporting information (Figs. S1 and S2). An equilibrium cell with an internal volume of 250 cm^3 was made of 316 stainless steel and was immersed in a water bath whose temperature was controlled

by an external circulator (RW-2025G, JEIO Tech, Republic of Korea.). A thermocouple with an accuracy of $\pm 0.1\text{ K}$ was used to measure the temperature of the cell. The contents in the cell were vigorously mixed by an impeller-type agitator. A pressure transducer (S-10, Wika, Germany) with an uncertainty of 0.01 MPa was used to measure the system pressure, and it was calibrated using a Heise Bourdon tube pressure gauge (CMM - 137219, Ashcroft Inc., USA) for the experimental range.

2.2. Hydrate phase equilibrium measurement

The equilibrium cell was initially filled with 50 cm^3 of the PZ or HZ solution. Several iterations of ventilation were conducted to purge the air in the remaining volume of the cell, and then, CH_4 gas was injected into the equilibrium cell until it reached the target pressure. Hydrate phase equilibria were measured under an isochoric condition with step heating and cooling. At first, the temperature of equilibrium cell was lowered at 1.0 K/h until gas hydrate was formed, and the hydrate formation could be detected by an abrupt pressure drop because gas hydrate can capture a large amount of gas molecules in the hydrate cages (Fig. S3). After 6 h for completion of gas hydrate formation, the temperature was increased at steps of 0.1 K/90 min for gas hydrate dissociation (Fig. S4). As the temperature increased, the cell pressure also increased due to gas molecules released from gas hydrate cages through dissociation. The pressure was slightly increased even after the hydrate was completely dissociated because of the thermal expansion of vapor phase. Using the pressure and temperature profiles during the hydrate formation and dissociation, the three-phase (hydrate (H) – liquid water (L_w) – vapor (V)) equilibrium point (point E in Fig. S3) was determined from the intersection point between the hydrate dissociation line and thermal expansion line at a specified pressure.

2.3. Spectroscopic analyses

A Bruker 400 MHz solid-state NMR spectrometer from the Korea Basic Science Institute (KBSI) was used to identify the structure and guest distribution of the CH_4 + diamine hydrates. The finely-powdered hydrate samples were loaded into a 4 mm o.d. Zr-rotor and analyzed at 243 K under atmospheric pressure. The ^{13}C NMR spectra were collected at a Larmor frequency of 100.6 MHz with a magic angle spinning (MAS) between 2 and 4 kHz. The downfield carbon resonance peak of adamantane (38.3 ppm at 300 K) was used as an external chemical shift reference. Two types of Raman spectrometers were used in this study: a micro Raman spectrometer (alpha 300R, WITech, Germany) and an in-situ fiber-coupled Raman spectrometer (SP550, Horiba, France). The pelletized hydrate sample was analyzed under atmospheric pressure at 153 K using a micro Raman spectrometer with a thermoelectrically-cooled CCD detector and 1800 grooves/mm holographic grating. In order to monitor the hydrate formation behavior and the enclathration of CH_4 gas in the hydrate cages, an in-situ fiber-coupled Raman spectrometer with a multichannel air cooled CCD detector and 1800 grooves/mm grating was used. Time-dependent Raman spectra during gas hydrate formation were collected using a fiber optic-Raman probe that was attached to the jacketed reactor. The reactor was pressurized to 9.0 MPa with CH_4 , and the pressure was maintained by a constant pressure mode of a syringe pump (ISCO 500D, Teledyne, USA). The subcooling temperature (ΔT), which is defined as the difference between the equilibrium temperature and the experimental temperature at a given pressure, for CH_4 hydrate formation was set to 6.0 K for monitoring growth patterns and 4.0 K for determining the induction time. A more detailed description of experimental apparatuses and methods are provided in our previous papers [31–34].

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