

Comprehensive Molecular Dynamics Simulation Study on the Phase Behavior, Inhibitory Mechanisms, and Synergistic Effects of Ethylene Glycol and Its Combination with PVP-A on Methane Hydrates under Multivariable Conditions

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論 文 名 : Comprehensive Molecular Dynamics Simulation Study on the Phase Behavior, Inhibitory Mechanisms, and Synergistic Effects of Ethylene Glycol and Its Combination with PVP-A on Methane Hydrates under Multivariable Conditions (多変数条件下におけるエチレングリコールおよび PVP-A との複合系がメタンハイドレートに及ぼす相挙動、抑制メカニズム、ならびに相乗効果に関する包括的な分子動力学シミュレーション研究)

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論 文 内 容 の 要 旨

Natural gas hydrates are crystalline compounds in which water molecules form cage-like structures through hydrogen bonding, encapsulating gas molecules within. The carbon content stored in hydrates across global oceans and permafrost is estimated to be more than twice the total known reserves of all fossil fuels, making them a highly promising clean energy resource. However, under specific temperature and pressure conditions, hydrates can spontaneously form and grow rapidly in extraction and transportation pipelines, leading to blockages, operational disruptions, and safety hazards—particularly in high-risk environments such as deep-sea and polar regions. Therefore, the effective inhibition of hydrate formation and growth is of critical importance to the oil and gas industry.

This study provides a theoretical foundation for the development of low-dosage, high-efficiency, and environmentally friendly hydrate inhibitors, and offers new perspectives and technical support for the green management of hydrate-related risks in deepwater oil and gas production. It holds significant theoretical value and practical engineering potential.

This dissertation is organized into 7 chapters as follows:

Chapter 1 addresses the urgent issue of inhibiting the growth of gas hydrates during extraction processes. It explains the rationale for selecting ethylene glycol and polyvinylpyrrolidone-acrylic acid copolymer (PVP-A) as the primary subjects of investigation. The current research progress on ethylene glycol is reviewed, particularly in relation to its effects on the hydrate phase equilibrium diagram, melting, formation, and growth. Furthermore, this chapter outlines the state of research on synergistic inhibition of hydrate formation, with a focus on the interactions between kinetic hydrate inhibitors (KHIs) and thermodynamic hydrate inhibitors (THIs), as well as those involving amino acids, ionic liquids, and polymers.

Chapter 2 outlines the theoretical foundations and technical methodologies underlying the molecular dynamics (MD) simulations conducted in this study. It covers the basic principles of MD and its advantages in capturing the evolution of microscopic structures, as well as the application of temperature and pressure control algorithms, mainstream general-purpose force fields, and time integration algorithms. In addition, the chapter discusses key analytical methods such as mean square displacement (MSD), radial distribution function (RDF), and system potential energy. The GROMACS simulation platform is also briefly introduced, establishing a solid technical basis for the successful implementation of the simulation work in this research.

Chapter 3 constructed a three-phase model consisting of a hydrate cage phase, a water – ethylene glycol phase, and a methane phase, where the ethylene glycol concentration was defined as its mass fraction in the water – ethylene glycol phase. The systems covered a range of concentrations from 0 wt% to 40 wt%. Methane, ethylene glycol, and water molecules were modeled using the OPLS-AA, CHARMM36, and TIP4P/Ice force fields, respectively. For ethylene glycol concentrations of 0, 1, 5, and 10 wt%, the pressure – temperature range for hydrate melting and the corresponding phase equilibrium diagrams were clearly determined. Furthermore, the effects of higher ethylene glycol concentrations were investigated, revealing a significant shift in inhibition performance between 15 wt% and 20 wt%.

Chapter 4 explores the effects of temperature, pressure, and ethylene glycol concentration on the melting behavior of methane hydrates. Simulation results indicate that increasing temperature significantly promotes hydrate melting, while higher system pressure effectively suppresses hydrate dissociation. In terms of ethylene glycol concentration, 15 wt% serves as a critical threshold: below this concentration, melting is inhibited, whereas above it, the melting process is markedly accelerated. During the melting process, ethylene glycol molecules initially accumulate at the interface between the hydrate phase and the water phase, then gradually migrate to the water – methane interface. The mechanisms by which ethylene glycol promotes melting primarily include the disruption of the hydrogen-bond network within the hydrate lattice, thereby reducing structural stability, and the acceleration of methane release from the hydrate cages.

Chapter 5 systematically explores the effects of temperature, pressure, and ethylene glycol concentration on the growth behavior of methane hydrates. The results indicate that, under identical conditions, an increase in temperature suppresses hydrate growth, whereas higher pressure promotes its formation. Additionally, the inhibitory effect becomes more pronounced with increasing ethylene glycol concentration. Mechanistically, ethylene glycol molecules initially accumulate at the interface between the hydrate and water phases, gradually migrate to the primary growth region, and ultimately localize within the internal voids of the hydrate structure. The inhibition is primarily attributed to a reduction in the thermodynamic stability region, disruption of the orderly arrangement of water molecules, and a decrease in water activity.

Chapter 6 reveals that the combined use of ethylene glycol and PVP-A significantly enhances hydrate inhibition. PVP-A adsorbs onto the crystal surface to form a protective film and disrupts the hydrogen bonding network of water molecules, thereby delaying hydrate formation. The synergistic effect is influenced by the mass ratio of PVP-A to ethylene glycol, with the optimal ratio observed at 1.7:1. Phase equilibrium diagrams indicate that even a small amount of ethylene glycol combined with PVP-A can exert thermodynamic inhibition, and increasing the proportion of ethylene glycol further lowers the equilibrium temperature. Additionally, simulations consistently show the spontaneous formation of methane bubbles, which reduce the concentration of free methane and hinder diffusion, thus providing an inhibitory effect.

Chapter 7 focuses on the synergistic inhibition mechanisms of glycol and PVP-A, providing a systematic analysis of the dual effects of glycol concentration on both hydrate formation and dissociation, along with its critical threshold. The nonlinear influences of temperature and pressure are discussed, as well as the synergistic performance of the two inhibitors at different mass ratios. In addition, the chapter examines the formation of methane bubbles and their indirect inhibitory role based on simulation results. Finally, the industrial significance, limitations of the study, and future research directions are presented.