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Molecular insight into the Inhibitory Effects of Amino Acids on Natural Gas Hydrate.

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Abstract

This study investigates the effectiveness of amino acid inhibitors (histidine, glycine, alanine, and proline) in preventing the formation of C1+C3 structure II hydrates, which are known to disrupt the flow of hydrocarbon transportation. Using GROMACS molecular dynamics simulations, the interaction between these amino acids and water molecules was analyzed under conditions conducive to sII hydrate formation. The analysis focused on parameters such as visualization and F3 and F4 order metrics, which suggest that lower values correspond to a liquid-like state, essential for confirming the effectiveness of the inhibitors. The results indicate that histidine and proline significantly inhibit hydrate formation, with histidine being the most effective, followed by proline. Glycine and alanine were found to be less effective. The study highlights the potential of histidine and proline as sustainable options for mitigating gas hydrate risks in pipelines and suggests a pathway toward environmentally friendly inhibition strategies in the oil and gas industry.

Keywords: amino acid; hydrate; inhibitor; perturbation; adsorption; mechanism.

Introduction

Gas hydrates are crystalline ice-like solids in which gas molecules, typically hydrocarbons, are trapped within cages of hydrogen-bonded water molecules [1]. These hydrates can form under high-pressure and low-temperature conditions commonly found in subsea pipelines and natural gas processing systems [2]. Among the various structures of gas hydrates, structure II (sII) is notably problematic in the energy industry due to its ability to encage large gas molecules, leading to blockages that disrupt the flow of oil and gas [3], [4], [5], [6]. These blockages can result in operational inefficiencies, increased maintenance costs, and heightened safety risks [7].

Traditionally, the formation of gas hydrates is mitigated using thermodynamic inhibitors such as methanol or glycol, which work by shifting the equilibrium conditions necessary for hydrate formation to a region of high temperature and pressure conditions [8], [9], [10]. However, these substances often pose environmental risks and economic burdens due to their high dosage requirements and potential toxicity [1]. This has driven research into alternative inhibitors that are both effective and environmentally benign.

Recent studies have highlighted amino acids as promising candidates for hydrate inhibition. Amino acids, the building blocks of proteins, offer several advantages as hydrate inhibitors [11], [12], [13], [14]. They are inherently biodegradable, less toxic, and potentially effective at lower concentrations compared to traditional inhibitors [2]. Moreover, their functional groups (amine and carboxyl) can form hydrogen bonds with water molecules, suggesting a possible mechanism for disrupting the hydrate formation process [14], [15].

Despite the potential benefits, the detailed molecular mechanisms through which amino acids inhibit hydrate formation are not fully understood. This gap in knowledge hinders the optimization and practical application of amino acid-based inhibitors in industrial settings. To address this, our study employs molecular dynamics simulations, specifically using the GROMACS software, to explore the interactions between amino acids and water molecules under conditions conducive to sII hydrate formation. The primary objective of this research is to investigate the inhibition mechanisms of histidine, glycine, alanine, and proline on C1+C3 hydrates. The specific objectives of the study aim to determine how these amino

acids interact with water molecules within the hydrate lattice and assess the impact of these interactions on the stability and integrity of the hydrate structure.

Methodology

Simulation Software and Setup

Molecular dynamics simulations were conducted using GROMAC version 2019.5, chosen for its ability to efficiently handle complex molecular systems. A preformed Structure II hydrate composed of 90% C1 and 10% C3 was embedded in a cubic box filled with TIP4P/Ice model water molecules, which was used as the simulation system, ensuring an accurate representation of water's properties under periodic boundary conditions. The OPLS-AA force field, a widely respected parameter set, was used to accurately describe the molecular interactions of C1+C3 hydrates and amino acids, ensuring realistic simulation outcomes. To account for the varied interactions between different types of molecules, such as water, C1+C3, and amino acids, the Lorentz-Berthelot mixing rules were applied. This approach calculates the potential interactions across different species, which is essential for understanding how these molecules interact within the hydrate formation process.

Selection and Incorporation of Amino Acids

Four different types of amino acids (glycine, histidine, alanine, and proline) were selected for their structural simplicity and potential influence on water interactions. These amino acids were introduced into the simulation box at a 1:5 molar ratio relative to the hydrate.

Simulation Conditions

Simulations were performed at 270 K and 10 MPa to reflect conditions typical in subsea gas pipelines. Each amino acid was simulated separately to isolate its effects on hydrate stability.

Equilibration and Production Runs

The simulation process included energy minimization, followed by several particles, volume, and temperature (NVT) and number of particles, pressure, and temperature (NPT) ensemble equilibrations. Production runs were carried out for 350 nanoseconds, with data sampling every 10 picoseconds.

Data collection and analysis

Key parameters analyzed included F3 and F4 order parameter calculation, hydrate cage identification and hydrate count calculation, mean square displacement (MSD), and radial distribution functions (RDFs). These metrics provided insights into the impact of amino acids on hydrate structure and stability [1].

Results and Discussion

The effectiveness of these amino acids as inhibitors was evaluated, with Fig. 1 providing visual evidence of their impact. It was observed that histidine had the most significant inhibitory effect, followed by proline, with glycine and alanine showing comparable levels of inhibition. This hierarchy of effectiveness histidine > proline > glycine = Alanine suggests that the ability of histidine and proline to adhere to the hydrate surface plays a crucial role in their inhibitory action. The underlying principle for this inhibition lies in the adsorption phenomenon, where molecules of histidine and proline attach themselves to the surface of the forming hydrate [1] (often referred to as the "slab"). This attachment disrupts the normal formation and growth process of the hydrate crystals, effectively slowing down or even preventing the development of natural gas hydrates [1][3]. The adsorption of these amino acids creates a barrier that interferes with the arrangement of water and gas molecules necessary for hydrate formation [3][4].

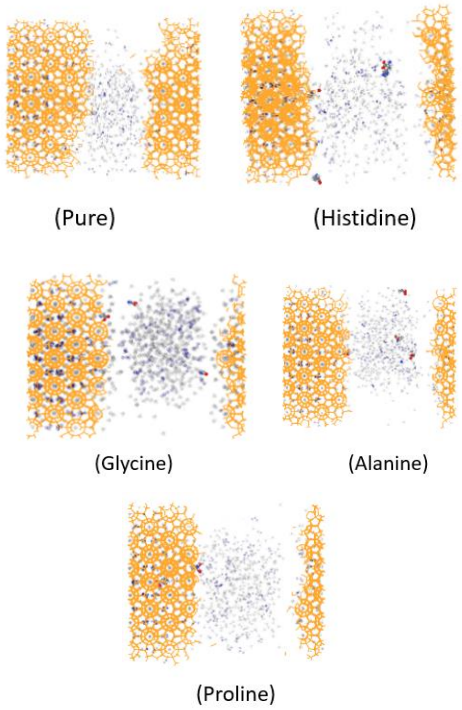

Figure 1. KHIs-Visualization for Pure water and Amino acids system.

Figure 2 shows how F4 order parameters and hydrate counts indicate the growth of C1+C3 hydrates, highlighting the effectiveness of amino acids in inhibiting natural gas hydrate formation by keeping more water molecules in a liquid state. While pure water systems showed complete sII

hydrate formation with an F4 value around 0.7, typical of fully formed structure II (sII) hydrates [1], systems with amino acids did not reach this F4 value within 350 ns, suggesting that amino acids delay hydrate formation. The research further analyzed F3 order parameters, showing that lower values are linked to a liquid-like state [1], thus confirming the inhibitory effects of amino acids, ranked histidine being the most effective, followed by proline, with glycine and alanine being equally less effective. This is particularly relevant for a gas mixture of 90% C1 and 10% C3.

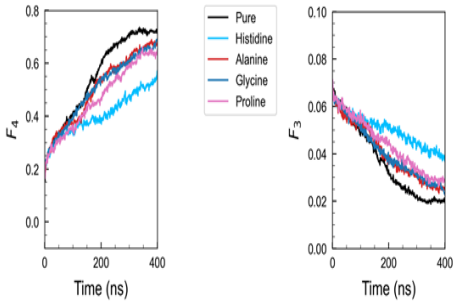

Figure 2. Order parameters (F4 and F3) for system water and amino acids system.

The analysis showed that C1+C3 molecules moved more than water molecules across all scenarios, with increased movement in systems containing amino acids, especially systems with histidine, indicating its significant effect on the mobility of both water and C1+C3 molecules. This enhanced mobility aids hydrate nucleation and growth. Molecular dynamics simulations confirm that histidine, as an inhibitor, promotes a greater presence of mobile liquid-like water and dynamic sII molecules. The effectiveness of amino acids as inhibitors is ranked with histidine as the most effective, followed by proline and alanine.

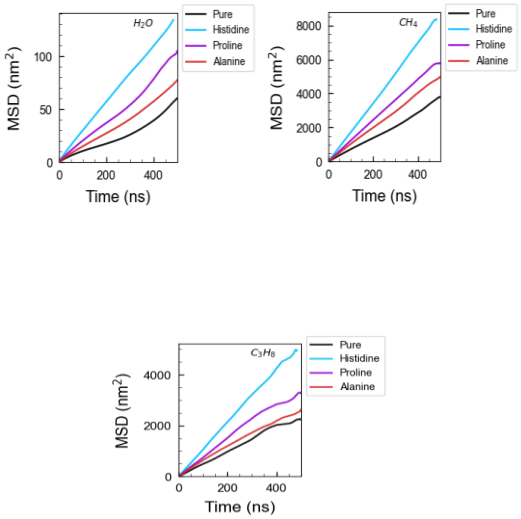

Figure 3. Mean Square Displacement for the pure water and amino acids system.

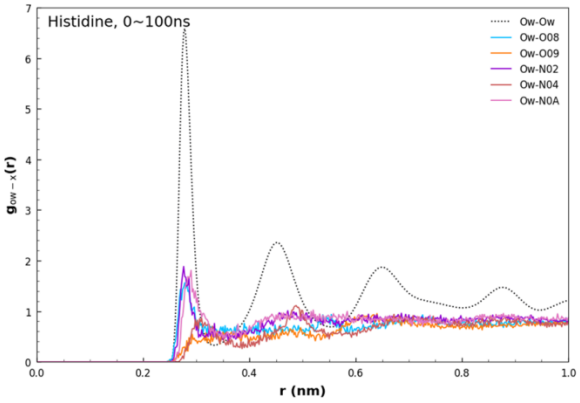

Figure 4. Radial Distribution Function (RDF) profile for 0.5wt% histidine.

The findings from Fig. 3 and Fig. 4 show that all tested amino acids significantly delay hydrate nucleation, with histidine having the most substantial impact with C1 and C3 molecules moving more vigorously than in the water molecules. The data from the simulations indicate that amino acids interfere with the hydrogen bonding network in water, preventing the formation of hydrate cages [1]. Energy calculations reveal that the interaction energies between amino acids and water molecules play a key role in their effectiveness as inhibitors [1]. The amino acids' ability to disrupt water structure points to a potential mechanism for hydrate inhibition, which seems to relate to the amino acids' hydrophobic nature and molecular size [3][5][6].

Conclusions

In MD simulations involving C1+C3 as sII-forming hydrate, histidine showed superior performance with an inhibition effect in descending order of performance as, histidine > proline > glycine = alanine. There is therefore an adsorption of histidine and proline onto the slab, which in turn is anticipated to improve performance.
This study confirms the potential of glycine and alanine to serve as sustainable inhibitors against the formation of C1+C3 hydrates. The insights gained from the molecular dynamics simulations highlight the critical role of amino acids in disrupting hydrate formation, suggesting a viable pathway toward developing more environmentally friendly inhibition strategies in the oil and gas industry. Further research is required to assess the practicality of using amino acid-based inhibitors in industrial settings.

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Responsibility Notice

Fawziyah Oyefunke Olarinoye: Conceptualization, Investigation, Writing – Original Draft, Data Curation, Formal Analysis, funding acquisition. Seong-Pil Kang: Resources, Software, Methodology, Writing–Review & Editing, Supervision.

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