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Molecular Dynamics Simulation of Nanoparticle Collaborating to Stabilize Carbon Dioxide Foam

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Abstract

CO_2 foam fracturing has been widely adopted in unconventional oil and gas exploration and development due to its low water consumption and effective reservoir enhancement. To investigate the impact of acidic environments caused by CO_2 dissolution on foam stability, this study selected two common surfactants: Octadearyl dimethyl ammonium chloride (OTAC), α-olefin sulfonic acid (AOS), and nano-silica SiO_2 particle. Using Materials Studio software to construct a foam liquid film model, this study investigates the compatibility and foam stabilization effects of cationic and anionic surfactants with nano-SiO_2 particles by comparing the diffusion behavior of water molecules in neutral versus acidic environments across different systems. Revealing the Mechanism of Acidic Environment on Synergistic Effect at Molecular Level. These findings provide theoretical foundations for optimizing CO_2 foam fracturing fluid formulations.

Keywords

Carbon Dioxide Foam; Nanoparticles; Surfactants; Molecular Dynamics Simulation.

1. Introduction

In recent years, as conventional oil and gas reservoirs have been increasingly developed, the exploration and development of unconventional oil and gas fields have become crucial for meeting global energy demands[1]. However, these reservoirs typically exhibit low porosity and permeability, and are predominantly located in mountainous, hilly, and desert regions with scarce water resources[2]. Traditional hydraulic fracturing technologies struggle to achieve large-scale application in such environments. Foam fracturing technology, as an emerging approach for unconventional oil and gas development, demonstrates significant potential in water conservation, environmental protection, and enhancing oil recovery[3]. CO_2 foam fracturing fluids combine low water consumption, minimal formation damage, and efficient fluid recovery[4], while also integrating oil and gas development with Carbon Capture, Utilization and Storage (CCUS) technology, making it a current research hotspot[1]. However, foam constitutes a thermodynamically unstable system, with spontaneous degradation severely compromising their performance. Their poor stability and short lifespan under high-temperature formation conditions significantly limit practical field applications. Therefore, improving the stability of CO_2 foam systems holds substantial practical significance.

To address the complex challenges of unconventional oil and gas reservoirs characterized by high temperature, high pressure, low porosity, and low permeability, the development of CO_2 foam fracturing fluids has progressed through three distinct phases[5]. The liquid phase of first-generation CO_2 foam fracturing fluids primarily consists of linear polymer foam stabilizers and foaming agents to enhance system stability and sand-carrying capacity. With the maturation of acid cross-linking technology, the second-generation system introduced cross-linked modified guar gum as the liquid phase component, achieving significantly improved foam viscosity and stability. The third-generation CO_2 foam fracturing fluids focused on controlling internal phase volume, where constant internal phase technology resolved high-sand ratio friction issues[7], while VES technology maintained over

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95% flow direction retention. To address the high cost and environmental concerns, recent research has leveraged the interfacial properties and scale effects of nanomaterials, synergizing with surfactants and other stabilizers[8]. Binks[10] et al. demonstrated that surfactant adsorption on gas-liquid film interfaces is reversible, with frequent molecular exchange between gas and liquid phases, whereas nanoparticles form irreversible adsorption on liquid films, exhibiting superior foam stabilization. Sun[11] et al. discovered that hydrophobic SiO_2 nanoparticles and anionic surfactant sodium dodecyl sulfate (SDS) can stably form foam through electrostatic interactions. Yekeen[12] et al. investigated the effects of nanoparticle blends with various surfactants on foam stability. Their findings revealed that electrostatic interactions between nanoparticle surface charges and surfactant head groups play a critical role in foam stability. These interactions enhance nanoparticle adsorption density at the gas-liquid interface, delay liquid drainage in foam systems, and improve foam stability. Zhu[13] et al. observed microstructural characteristics of nano-SiO_2-reinforced VES foam under cryo-SEM at different temperatures. They discovered that nano-SiO_2 further connects fine worm-like micelles, facilitating the formation of robust particle-micelle networks. Due to experimental limitations, complete microscopic visualization of surfactant aggregation patterns and adsorption configurations at interfaces remains challenging. With advancements in computational modeling and theoretical frameworks, researchers have employed molecular dynamics simulations to track dynamic evolution processes in complex systems, revealing molecular adsorption mechanisms and interaction principles at microscopic scales. Jang[14] et al. investigated calcium ion concentration effects on foam stability using molecular dynamics simulations. The results aligned with experimental data, demonstrating that surfactant foam stability is minimally affected by calcium ions through enhanced short-range interaction structures. Chanda[15] et al. investigated the physical properties of surfactants at oil/water and gas/water interfaces through molecular dynamics simulations. Their findings revealed that the carbon chain tails of surfactants exhibit more perpendicular alignment at oil/water interfaces. However, there is limited research on the synergistic stabilization mechanism of ionic surfactants and nanoparticles in CO_2 foam, and the impact of the acidic environment resulting from CO_2 dissolution in water on this synergistic effect has not been considered.

This study investigates the interfacial adsorption behavior and synergistic foam stabilization mechanism of cationic (OTAC) and anionic (AOS) surfactants with SiO_2 nanoparticles under different pH conditions through Materials Studio (MS) molecular dynamics simulations, revealing their impact on foam stability.

2. Establishment and Simulation Method of Foam Liquid Film Model

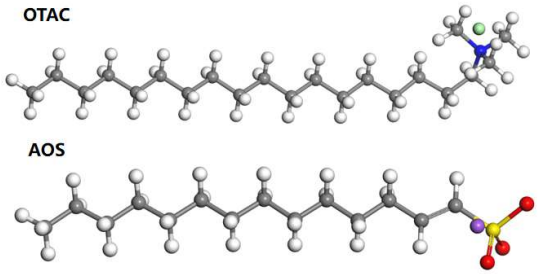

Figure 1. Molecular models of OTAC and AOS

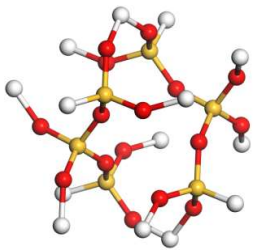

Figure 2. SiO_2 nanoparticle model

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The study selected common cationic surfactant Octadearyl dimethyl ammonium chloride (OTAC) and anionic surfactant α-olefin sulfonic acid (AOS) as research subjects. Molecular modeling was performed using MS software as shown in Figure 1, followed by structural optimization with the Forcite module. A water layer simulation was constructed using the Amorphous Cell module, containing 1,000 H_2O molecules, dissociated salt ions, and acid radicals in aqueous solution at a density of 1 g/cm^3. The Build Nanostructure module was employed to construct spherical SiO_2 nanoparticle models with a radius of 4 Å, featuring hydroxyl-saturated facets, as illustrated in Figure 2.

Based on the foam liquid film "sandwich" model developed by Gamba et al.[16], the Build Layers module integrates the surfactant layer, nanoparticle layer, and water layer. The hydrophilic head groups of the surfactant face the water layer surface, while the hydrophobic chains extend toward the vacuum, forming a miniature foam liquid film model as shown in Figure 3. This model elucidates the macroscopic behavior of foam systems through microscopic structural analysis.

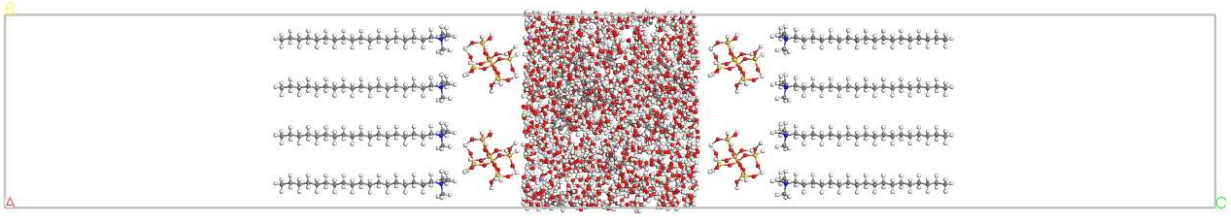

Figure 3. Foam liquid film model

The simulation employed the COMPASS III force field and utilized the Smart method for structural optimization. The optimized model was subjected to 200 ps dynamics equilibrium simulations under the NVT ensemble and Andersen method at 333.15 K. With a time step of 1 fs, the system's trajectory data was recorded every 2 ps. The equilibrium time was determined by tracking the mean square displacement (MSD) over time, and the remaining trajectory files were subsequently used for structural and kinetic analyses.

3. Result Analysis

The mean square displacement (MSD) can be used to characterize the movement amplitude and diffusion law of particles. The movement and diffusion of water molecules in the model can be studied by using the mean square root displacement, and the diffusion coefficient of water molecules can be calculated. The binding ability of different complex systems to water molecules can be studied, and the stability of foam can be deduced.

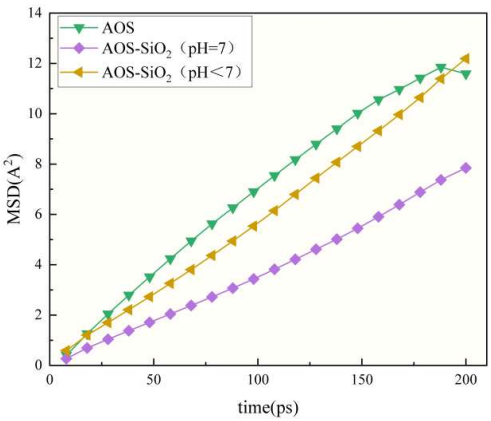

Figure 4. Mean Square Deviation of Water Molecules in the AOS System Perpendicular to the Liquid Film

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As shown in Figure 4, the addition of nano-SiO_2 particles in a neutral environment effectively reduces the mean square deviation (MSD) of water molecules perpendicular to the liquid film direction in the AOS system, thereby decreasing water diffusion rates and enhancing foam stability. This occurs because anionic surfactants ionize in water to form negatively charged anions with surface activity. The hydroxyl-saturated hydrophilic nano-SiO_2 particles carry negative charges in aqueous solutions, creating electrostatic repulsion that induces steric hindrance. This restricts water molecule diffusion and prevents adjacent bubbles from merging, thus improving stability. In acidic environments, however, the abundant H^+ ions in the solution combine with anions within the system, thereby compromising foam stabilization.

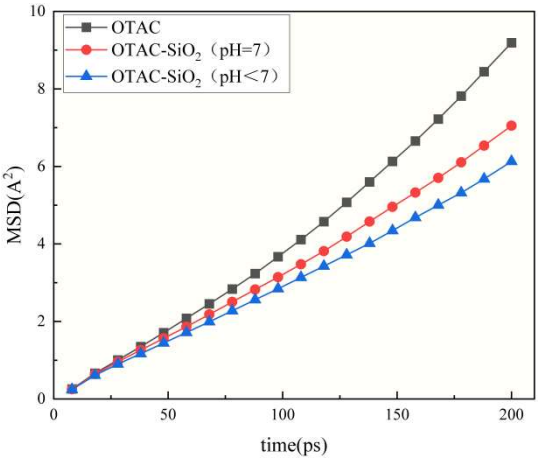

Figure 5. Mean Square Deviation of Water Molecules in the OTAC System Perpendicular to the Liquid Film

As illustrated in Figure 5, the incorporation of nano-SiO_2 particles in neutral environments effectively reduces the mean square deviation (MSD) of water molecules perpendicular to the liquid film direction in the OTAC system, thereby decreasing water diffusion rates and enhancing foam stability. This mechanism stems from the formation of surface-active cations when cationic surfactants ionize in water. The hydroxyl-saturated hydrophilic nano-SiO_2 particles acquire negative charges in aqueous solutions, where electrostatic attraction and hydrophobic interactions form stable structures that restrict water diffusion, ultimately improving foam stability. Notably, in acidic conditions, the presence of abundant H^+ ions in the solution does not compromise foam stabilization. The schematic diagram of this principle is shown in Figure 6.

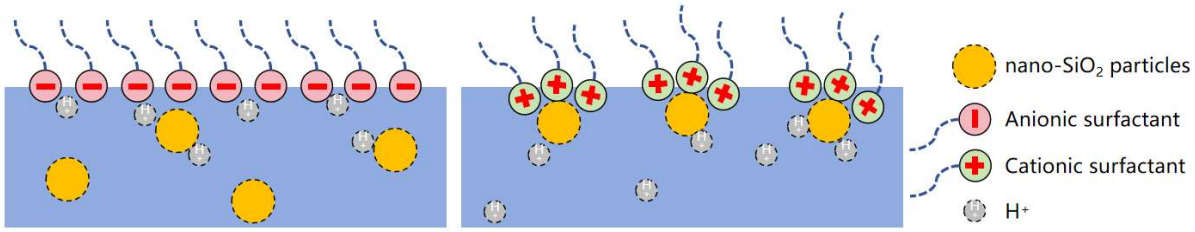

Figure 6. Schematic diagram of different mixed systems

As shown in Figure 7, the comprehensive comparison of the MSD functions of water molecules perpendicular to the liquid film direction in both systems demonstrates that the cationic surfactant system exhibits stronger compatibility with hydrophilic nano-SiO_2 particles. It effectively restricts water molecule diffusion and is less affected by the acidic environment created by CO_2 dissolution in water.

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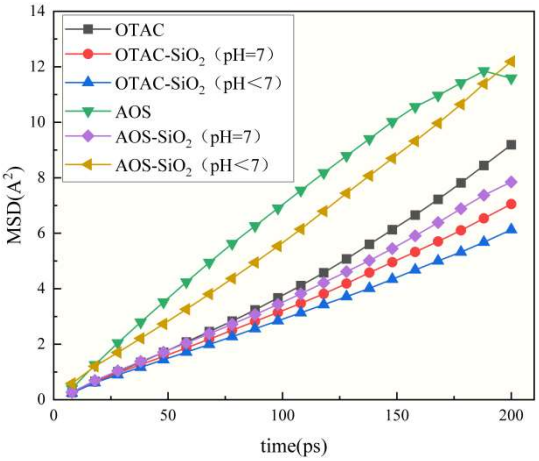

Figure 7. Mean Square Deviation of Water Molecules Perpendicular to the liquid film direction in different systems

4. Conclusion

The acidic environment created by CO_2 dissolution in water may compromise the synergistic stabilization of CO_2 foam by surfactants and nanoparticles. Therefore, when developing optimized CO_2 foam fracturing fluid formulations, the impact of acidic conditions on system synergy must be thoroughly evaluated.

The hydrophilic nano-SiO_2 particles have negative head charge, which can increase the space steric hindrance of the liquid film by electrostatic repulsion with the head of anionic surfactant AOS, thus improving the stability of the foam. However, the effect is weak and the synergistic effect is easily lost under the influence of H^+ in acidic environment.

The hydrophilic nano-SiO_2 particles, with their head groups carrying negative charges, adhere to the head groups of the cationic surfactant OTAC. This interaction promotes more orderly alignment of OTAC molecules at the gas-liquid interface, thereby enhancing their binding capacity for water molecules. The adsorption also confers hydrophobicity to the nanoparticles, while the particles themselves further contribute to water molecule binding. Remarkably, this synergistic effect persists even under acidic conditions.

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