Analyzing Cage Occupancy Rates in Structure II Clathrate Hydrates Using Gibbs Ensemble Monte Carlo Simulations

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Clathrate hydrates, hereafter referred to as hydrates, are molecular crystals characterized by a cage-like structure formed through hydrogen bonding between water molecules. This structure endows hydrates with guest selectivity. Typically, the presence of guest molecules enables hydrates to maintain a stable crystal structure, with the thermodynamic properties and crystal structures varying depending on the type of guest molecule. Therefore, understanding the guest molecule occupying mechanism at the molecular scale is crucial in advancing our comprehension of hydrates. The Gibbs Ensemble Monte Carlo (GEMC) method, a molecular simulation technique, allows for realistic calculations of cage occupancy ratios through the probabilistic movement of molecules. This study focuses on bulk systems of hydrates in equilibrium with mixed-phase systems of propane and carbon dioxide, employing the GEMC method to calculate the cage occupancy ratios of guest molecules. Interestingly, it was found that carbon dioxide exhibits increased cage occupancy ratios under high pressure and low temperature conditions where hydrates are stable, while propane shows enhanced cage occupancy ratios under low pressure and high temperature. This phenomenon can be attributed to cage volume changes in the Structure II hydrates, making it difficult for carbon dioxide to occupy the smaller cages. The aim of this research is to elucidate the intriguing effects that guest molecules have on cage occupancy ratios in Structure II hydrates, from the perspectives of temperature-pressure dependency and cage volume changes.