Elucidation of Potent Methane Clathrate Stabilizing Agents by Means of Molecular Dynamics, Effective Fragment Potential Method and Density Functional Theory

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Storage and transportation of methane in form of methane clathrates represent promising, more ecologically-friendly and cost-efficient alternative to conventional approaches currently used in natural gas industry. The economic feasibility of methane clathrates as the methane carrier is constrained by the fact that methane clathrates are stable only at temperatures below 0ÂºC, which leads to additional costs associated with the cooling of methane clathrates. To reduce these costs one can introduce the stabilizing agent that could be added to mixture of methane and water during crystallization of methane clathrates. Such stabilizing agent would increase the strength of binding interactions within the methane clathrate crystals and elevate the freezing point above 0ÂºC. Moreover, the elucidation of potent and inexpensive compounds capable of increasing the freezing point of methane clathrates would not only have economic impact on natural gas industry, but also would help to resolve one of the major environmental protection problems associated with melting of natural deposits of methane clathrates.

In order to find candidate compounds, we developed methodology that combines classic force-field molecular dynamics (MD) simulations with effective fragment potential (EFP) and density functional theory (DFT) geometry optimizations. Initial step in this methodology is the DFT geometry optimization of a single cage of methane clathrate doped with the candidate compound. Upon establishing stability of the substituted cage we proceed with the DFT geometry optimization of two adjacent methane clathrate cages where candidate compound interfaces two cages. This step is followed by EFP geometry optimization of the periodic box containing doped methane clathrate cages. In case if doped structures appear stable in all of the above calculations, we proceed with the molecular dynamics simulations of direct coexistence of the solid-liquid interface, which allows us to elucidate the change in melting point of the methane clathrate upon the introduction of the candidate compound. By having the binding energies obtained from DFT and EFP calculations we correlate the change in melting point to specific interactions within the crystal structures of doped methane clathrates, which allows us not only to find potent stabilizing agents, but also explain the mechanism behind this stabilization.