Structural Transition from Semi- to True Clathrate Hydrates Induced by Adding a Help Gas

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Diethylamine and n-propylamine known as semi-clathrate hydrate formers are found to show structural transition when inducing a help gas, CH4. The diethylamine·8.67H2O semi-clathrate hydrates (orthorhombic Pbcn) were changed to sH type (hexagonal P6/mmm) true clathrate hydrates, while the n-propylamine·6.5H2O semi-clathrate hydrates (monoclinic P21/n) turned to sII clathrate hydrates (cubic Fd3m). Different shape of large voids in the semi-clathrate hydrates changed to typical shape of sH or sII large voids, and pentagonal dodecahedra were formed so as to capture CH4 molecules. Transition pattern and molecular behaviour from semi-clathrate hydrate to true clathrate hydrates were analyzed by means of microscopic methods. In addition to microscopic analysis for transformed hydrate samples, three-phase (L-H-V) equilibrium conditions were also measured in order to identify thermodynamic effect of the guest species. The abnormal phase transition is exteded to a variety of alkylamine semi-clathrate hydrates, enabling the discovery of more precise physicochemical backgrounds in research field related water and ice materials.