STRUCTURAL STABILITY OF \((t\text{-}BuNH}_2+H_2/CH_4)\) BINARY HYDRATES

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ABSTRACT
Gas hydrates (clathrate hydrates) are nonstoichiometric inclusion compounds in which guest
molecules are trapped in a host lattice formed by water molecules in an ice-like hydrogen-bonded
framework. These are often materials for fuel gas storage and transportation applications. Clathrate hydrates with different structures (sI through sVII) are known and in particular sVI,
formed by the tert-butylamine \((t\text{-}BuNH}_2)\), is important because of its potential superior fuel gas
storage capacity. However, the critical issue hydrates with \(t\text{-}BuNH}_2\) is on the stability of the sVI
structure upon populating the vacant \(4^{5} 4^{4}\) cages in the structure with a small guest in the binary
hydrate. In this study we used hydrogen \((H_2)\) and methane \((CH_4)\) as co-guests and the structural
details of binary hydrates were analyzed using powder x-ray diffraction (PXRD) and micro-
Raman spectroscopy. The results demonstrate that the structural transformation (sVI to sII) of \(t\text{-}BuNH}_2\) hydrate pressurized with \(H_2\) or \(CH_4\) was clearly observed from the PXRD patterns. From
the molecular size considerations, \(CH_4\) is slightly too large for the \(4^{5} 4^{4}\) cages, whereas \(H_2\) is
suitable to occupy these small cages. However, experimental results indicate that the resulting
structure for the binary hydrates with \(t\text{-}BuNH}_2\) has always been sII with \(t\text{-}BuNH}_2\) in the \(5^{12} 6^{4}\)
cages and the smaller guest molecules \((H_2/CH_4)\) enclathrated predominantly in the \(5^{12}\) cages.
Experiments with powders of ice and solid \(t\text{-}BuNH}_2\) as reactants did not help the preven-
tion of the structural transformation. All our experiments indicate that sVI is unstable when pressurized with
co-guest molecules \((H_2/CH_4)\) in binary hydrates.

Keywords: gas hydrates, Binary hydrates; Hydrogen \((H_2)\); Methane \((CH_4)\); Structural
transformations; sVI; PXRD; Raman Spectroscopy

INTRODUCTION
Gas hydrates (clathrate hydrates) are non-stoichiometric inclusion compounds in which gaseous guest molecules are trapped in a host lattice formed by water molecules in an ice-like hydrogen-bonded framework. Gas hydrates exist
as a stable solid phase in permafrost regions and in
ocean-floor sediments around the world [1].
Substantial amounts of natural gas (mostly methane) are trapped in condensed form in
hydrates (typically \(1\ m^3\) of hydrate has \(164\ m^3\) of STP equivalent methane). In hydrate applications of energy recovery, transportation, and storage it