

## Complex Structure Transition of Pure and Mixed Ionic Clathrate Hydrates

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We report an extraordinary structural transition accompanying the occurrence of more than two coexisting clathrate hydrate phases in the mixed ionic ( $\text{CH}_4$  + tetramethylammonium hydroxide ( $\text{Me}_4\text{NOH}$ )) hydrate system. The changing structure of ionic ( $\text{CH}_4$  +  $\text{Me}_4\text{NOH}$ ) hydrate was investigated by NMR spectroscopy, and lattice structure information was obtained by assigning the structure-specific chemical shifts from  $^{13}\text{C}$  NMR spectra. In addition, the structures of the ionic hydrates identified from NMR spectroscopy were confirmed by using powder X-ray diffraction (PXRD). From the  $^{13}\text{C}$  NMR spectra, it is confirmed that structure-I (sI) and structure-II (sII) hydrates are dominant when water concentration is more than 16.0 mol  $\text{H}_2\text{O}$  per 1.0 mol  $\text{Me}_4\text{NOH}$  (16.0  $\text{H}_2\text{O}$ ). Significantly, quiet small signals from  $\text{CH}_4$  in large cages of sI and sII hydrates, compared to ideal distributions of  $\text{CH}_4$  in sI and sII cages, imply that  $\text{Me}_4\text{N}^+$  is enclosed in both sI-L and sII-L at the higher degree of hydration, and sII preference of cationic guest can be also confirmed by the  $^1\text{H}$  NMR spectra. PXRD patterns and  $^{13}\text{C}$  NMR spectra reveal the complex structure transition of ionic ( $\text{CH}_4$  +  $\text{Me}_4\text{NOH}$ ) clathrate hydrate as a function of water concentration.