METASTABILITY PHENOMENA OF ETHANE HYDRATE INDUCED BY COBAL COMPLEX AND BASE

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ABSTRACT

The metastability phenomenon of clathrate hydrates is of interest to researchers because of the formation/dissociation behavior due to distinctive structural transitions, complex phase behavior by molecular reorientation and practical process development for gas hydrate production. For the exploration of metastable structure patterns, ethane-related clathrate hydrate has been a focal point of active research. Because the ion effect on metastable hydrate structures has not yet been well examined, among various types of ionic coordination compounds, considering ion size and NMR sensitivity, we selected a hexamminecobalt(III) complex and examined its effect on the appearance of metastable hydrates. The $^{13}$C NMR spectra of $\text{C}_2\text{H}_6 + ([\text{Co(NH}_3]_6\text{Cl}_3 + 6\text{NaOH in D}_2\text{O})$ hydrate confirmed a new peak at 6.5 ppm which behaved as metastable phase. This phase is appeared only the coordination compound is in the presence of its counter anions such as OH− or F−. Also, area ratio of stable/metastable phase is totally reversed then recovered, which is noteworthy phenomenon compared to other researches which show existence of a little amount of metastable phase. This metastability phenomenon is different from formal studies in that metastable phase occurs at the middle stage of formation rather at the initial stage. The retarded appearance of metastable sII phase is due to brine rejection of the cobalt complex occurring during solution freezing. The anions of OH− and F− were found to be incorporated in the host water cage framework, providing proton-deficient sites. This anion-induced structural modification can improve the ionic conductivity, particularly given that the host framework is able to function as a pathway to deliver protons or electrons. The ionic conductivity of the frozen [Co(NH$_3$)$_6$]$^{3+}$ solution increased up to 20-fold after ethane hydrate formation, implying the incorporation of F− into the host lattice. From above, we cautiously suggest that the incorporation of anions in ionic clathrate hydrate should accompany the enclathration of counter cations, causing the occurrence of metastable sII phase. However, the physicochemical pathway for

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Proceedings of the 7th International Conference on Gas Hydrates (ICGH 2011),
Edinburgh, Scotland, United Kingdom, July 17-21, 2011.