PB 13

Thermodynamic stabilities of clathrate hydrates including tetrahydrofuran and quaternary onium salts

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Abstract (less than 300 words)

Tetrahydrofuran (THF), one of the most popular clathrate hydrate formers, forms the structure-II (sII) hydrate at temperatures below 277.5 K and atmospheric pressure. The sII unit lattice consists of 16 small cages (S-cages) as well as 8 large cages (L-cages). A THF molecule occupies the L-cage, whereas the S-cage remains vacant. The application of vacant S-cages, that is, the enclathration of another guest species into S-cages, has been investigated in the fields of gas separation or storage media. Considering the application of clathrate hydrates as latent heat storage materials, the enclathration of another guest species into vacant S-cages would be essential because it should lead to the increases in decomposition temperature and decomposition enthalpy of clathrate hydrates. It has been reported that, as a guest species other than small gas molecules, tetra-*n*-propylammonium fluoride (N3333F) can be enclathrated in the sII clathrate hydrate with THF (Manakov *et al.*, *J. Incl. Phenom. Mol. Recogn. Chem.*, vol. 17, pp. 99-106 (1994)). In the present study, we investigated thermodynamic stabilities of (THF + quaternary onium salt) mixed hydrates. The characterization of the (THF + quaternary onium salt) mixed hydrates was done with differential scanning calorimeter, Raman spectrometer, and powder X-ray diffractometer.

MTMS '21