

Measurement of Phase Equilibria and Dissociation Enthalpies of Semiclathrate Hydrate Conditions for Ionic Liquid Aqueous Solution with CH₄, CO₂ and H₂

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(kks1114@ut.ac.kr*)

This work reports the phase equilibrium boundary of tri-*n*-butylphosphine oxide (TBPO) semiclathrate hydrates incorporated with CH₄, CO₂ and H₂. Experiments were performed by isochoric method within the range of temperatures from 280 to 296 K and pressure from 1 to 11 MPa by a cylindrical vessel that is made of stainless steel 316 having an outer diameter of 6 cm and height of 5.5 cm (inner volume, V inner of 155 cm³). TBPO aqueous solutions with a molality (*m*) of (1.61 and 1.98) mol·kg⁻¹ were used for hydrate formation. The phase boundary at both concentrations was shifted to mild conditions which are lower pressures and higher temperatures, compared to each simple gas hydrate. In particular, TBPO + CO₂ double hydrate presented mild hydrate stabilization conditions of < 1 MPa at (280 to 285) K. Additionally, the dissociation enthalpy (ΔH_d) calculated from the phase boundary curves for the TBPO + CO₂ double hydrates was almost the same as that for tetra-*n*-butylammonium bromide (TBAB) + CO₂ double hydrate (219.5 kJ·mol⁻¹ for *m* = 1.61 mol·kg⁻¹ and 211.6 kJ·mol⁻¹ for *m* = 1.98 mol·kg⁻¹).