

Phase Equilibria and Dissociation Enthalpies of Tri-*n*-butylphosphine Oxide Semiclathrate Hydrates Incorporated with CH<sub>4</sub>, CO<sub>2</sub>, and H<sub>2</sub>

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We investigated the phase equilibrium boundary of tri-*n*-butylphosphine oxide (TBPO) semiclathrate hydrates incorporated with CH<sub>4</sub>, CO<sub>2</sub>, and H<sub>2</sub>. TBPO aqueous solutions with a molality (*m*) of (1.61 and 1.98) mol•kg<sup>-1</sup> were used for hydrate formation, which corresponded to the clathrate structures of TBPO•34.5H<sub>2</sub>O and 28H<sub>2</sub>O, respectively. The phase boundary at both concentrations was shifted to the promotion region represented by lower pressures and higher temperatures, compared to each simple gas hydrate. In particular, TBPO + CO<sub>2</sub> double hydrate presented mild hydrate stabilization conditions less than 1 MPa at (280 to 285) K. Additionally, the dissociation enthalpy ( $\Delta H_d$ ) calculated from the phase boundary curves for the TBPO + CO<sub>2</sub> double hydrates was almost the same as that for tetra-*n*-butylammonium bromide (TBAB) + CO<sub>2</sub> double hydrate (219.5 kJ•mol<sup>-1</sup> for *m* = 1.61 mol•kg<sup>-1</sup> and 211.6 kJ•mol<sup>-1</sup> for *m* = 1.98 mol•kg<sup>-1</sup>). These results demonstrate that the TBPO + CO<sub>2</sub> double hydrate could be used as refrigerants for cold storage and transportation.