

Hydrate phase equilibria for CO₂, CH₄, or N₂ + tetrabutylphosphonium bromide (TBPB) aqueous solution



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ABSTRACT

The phase behavior of tetrabutylphosphonium bromide (TBPB) semi-clathrates with three gases, viz. CO₂, CH₄ or N₂ was investigated in this study. The measurements were performed using a static high pressure cell using the isochoric pressure search technique. In order to determine the thermodynamic stability conditions of the semi-clathrates, the equilibrium data were measured at various concentrations of TBPB, viz. (0.05, 0.075, 0.10, 0.15, and 0.20) mass fraction TBPB. Measurements were undertaken in the temperature range of (279.3–291.4) K and in the pressure range of (1.06–7.79) MPa. The results indicate that TBPB has a promotion effect on semi-clathrate hydrate formation for the pure gas systems under consideration.

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1. Introduction

Clathrate hydrates (gas hydrates) are ice-like material composed of water and small gas/volatile liquid molecules. The water molecules form a hydrogen bonded framework or cage-like structure which encages the small gas/volatile liquid molecules [1,2]. In recent years, clathrate hydrates have attracted significant attention due to their application in carbon dioxide capture and storage [3–5], cold storage for air conditioning systems [6], separation of different gases [7], etc.

Moderate operating conditions are sought for the application of hydrate technology and this has been the focus of many literature studies. Quaternary ammonium salts (QAS) and phosphonium salts (QPS) which are generally used to promote gas hydrate formation form semi-clathrate hydrates. Measurements for flue gas

components with QAS and QPS are available in literature for tetrabutylammonium bromide semiclathrate hydrate (TBAB) [8–10], tetrabutylammonium fluoride (TBAF) [8,10], tetrabutyl ammonium nitrate (TBANO₃) [11], and tetrabutylphosphonium bromide (TBPB) [12].

Mayoufi et al. [13,14] utilized differential scanning calorimetry (DSC) to investigate the hydrate dissociation conditions and claimed that semi-clathrate hydrates can be used in secondary refrigeration, and gas capture and sequestration applications. Fujisawa et al. [15] studied the thermodynamic stability of H₂ + TBPB semi-clathrate hydrates and applied Raman spectroscopy to investigate the small-cage tendency of H₂ in mixed semi-clathrate hydrates. Li et al. [16] used TBPB to promote CO₂ capture from CO₂/N₂ binary mixtures. Suginaka et al. [17] experimentally investigated the thermodynamic properties, including the composition–temperature phase diagram and the dissociation enthalpy of semi-clathrate hydrates formed with TBPB. In another study, these authors measured the hydrate dissociation conditions of CO₂, CH₄, or N₂ + TBPB semi-clathrate hydrates at 0.35 mass fraction TBPB [12]. Shi et al. [18] measured the hydrate dissociation conditions for CO₂ and N₂ + TBPB semi-clathrate hydrates. They

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Table 1
Purities and supplier details of the chemicals used in this study.

Chemical	Formula	Purity	Supplier
Carbon dioxide	CO ₂	≥99.99 (vol %)	AFROX Ltd
Methane	CH ₄	≥99.99 (vol %)	AFROX Ltd
Nitrogen	N ₂	≥99.99 (vol %)	AFROX Ltd
Tetrabutyl phosphonium bromide (TBPB)	C ₁₆ H ₃₆ BrP	98% (mass fraction)	Sigma–Aldrich

investigated the promotion effect of TBPB at different concentrations of TBPB (0.050, 0.100, 0.371, and 0.600 mass fraction). They showed that a maximum stabilization effect was achieved with a 0.371 mass fraction TBPB solution. Zhang et al. [19] studied the hydrate dissociation conditions of TBPB hydrates with and without CO₂ in salt solutions of (0.10, 0.20, 0.35, and 0.50) mass fractions TBPB. Thereafter, they proposed visual observation of TBPB hydrate crystals and indicated that at high concentrations of TBPB, the crystal morphologies of CO₂ + TBPB double hydrates exhibit a leaf-shaped pattern.

In this study, phase equilibrium data (dissociation conditions) were measured for semi-clathrate hydrates of CO₂ + TBPB at (0, 0.05 and 0.15) mass fraction of TBPB in aqueous solution, CH₄ + TBPB at (0.10, 0.15 and 0.20) mass fraction of TBPB in aqueous solution, and N₂ + TBPB at (0.075, 0.10 and 0.20) mass fraction of TBPB in aqueous solution. The temperature ranges for these systems are (279.3–289.3) K, (287.2–291.4) K and (281.5–289.0) K respectively, and the pressures ranges are (1.06–4.45) MPa,

(2.74–6.91) MPa, and (2.43–7.69) MPa respectively.

2. Experimental

2.1. Materials

Table 1 lists the details of the suppliers and purities of chemicals used in this study. Ultrapure Millipore Q water with an electrical conductivity of 18 MΩ cm was used to prepare the TBPB aqueous solutions for all experiments.

2.2. Apparatus

A schematic diagram of the apparatus used in this study is shown in Fig. 1. The main part of the apparatus is a cylindrical equilibrium cell which has a volume of approximately 64 cm³. The cell is constructed of 316 stainless steel to withstand the high pressures required for hydrate measurements. The equilibrium cell

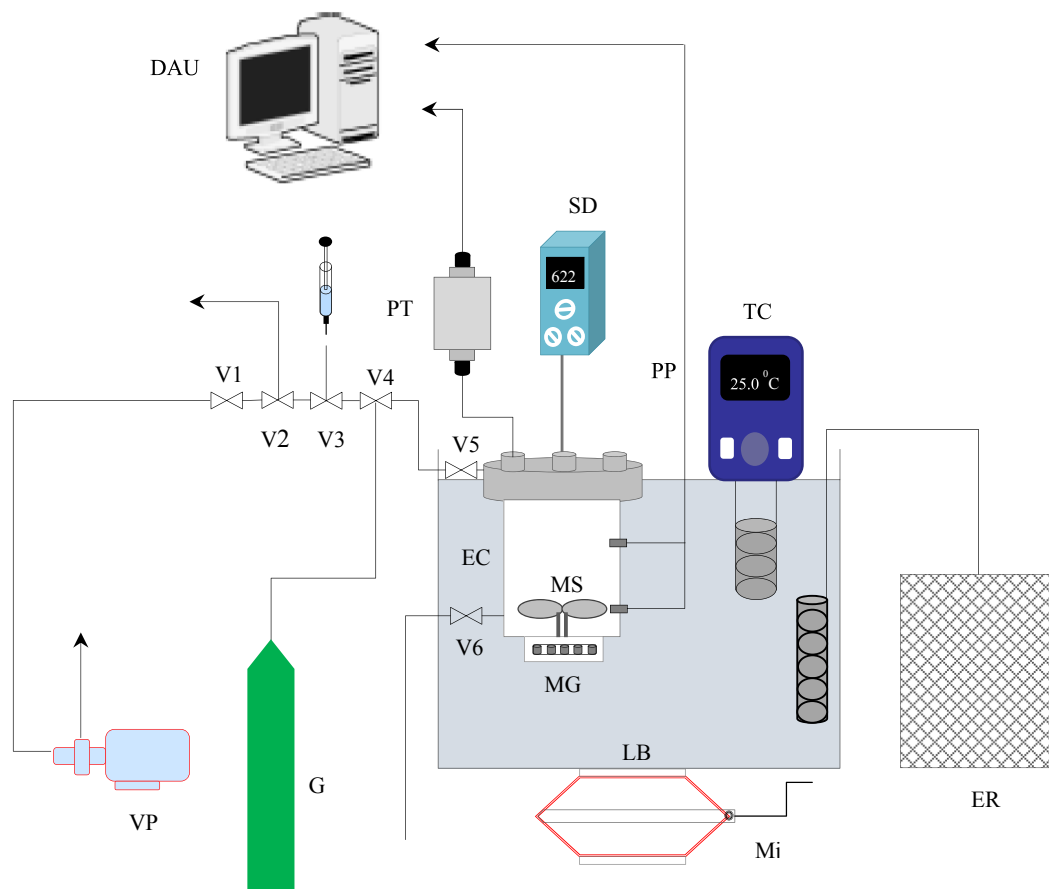


Fig. 1. Schematic diagram of the experimental setup: G, gas cylinder; LB, liquid bath; DAU, data acquisition unit; EC, equilibrium cell; ER, external refrigerator; TC, temperature controller; PT, pressure transducer; PP, platinum Probes; SD, stirring device; MS, magnetic stirrer; MG, mechanical gear; Mi, mechanical jack; VP, vacuum pump; V1, vacuum valve; V2, vent valve; V4, V5, feeding valves; V3, loading valve; V6, drain valves.

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