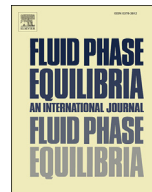




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Experimental measurements and modeling of the dissociation conditions of semiclathrate hydrates of tetrabutyl ammonium nitrate and carbon dioxide

Ponnivalavan Babu ^a, Patrice Paricaud ^b, Praveen Linga ^{a,*}

^a Department of Chemical and Biomolecular Engineering, National University of Singapore, 117585, Singapore

^b UCP, NSTA-ParisTech, Université Paris-Saclay, 828 Boulevard des Maréchaux, 91762 Palaiseau, France

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ABSTRACT

In this study, the mixed semiclathrate hydrate phase equilibrium condition of carbon dioxide in presence of various concentrations of TBANO₃ solution was determined using isochoric method. The mole fractions of TBANO₃ employed were 0.5, 1.0 and 3.0%. The presence of TBANO₃ reduces the hydrate phase equilibrium of CO₂ considerably. Increase in concentration of TBANO₃ decreases the mixed semiclathrate hydrate formation conditions. From the equilibrium data, enthalpy of dissociation of the mixed semiclathrate hydrate was calculated using the Clausius–Clapeyron equation. The calculated enthalpy of dissociation for mixed semiclathrate hydrate with various concentration employed in this study were similar suggesting formation of same type of semiclathrate hydrate structure (type b). The thermodynamic model of Paricaud [J. Phys. Chem. B 2011, 115, 288–299] was extended to fit the new experimental data.

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1. Introduction

The demand for power required for residential air conditioning is increasing in many countries. Air conditioning with cold storage systems can shift the demand to off-peak period and contribute for the loading levelling of power generation. Gas hydrates are attractive as cold storage media instead of water and ice due to its high cold storage density, higher chiller efficiency and elevated phase change temperature [1–3]. Gas hydrates are crystalline, non-stoichiometric compounds formed when a suitable guest molecule gets entrapped in the cavities formed by water molecules at a suitable temperature and pressure conditions [4,5]. The suitable guest molecule can be methane, carbon dioxide, hydrogen, etc. Gas hydrates exists in three different structures, namely cubic structure I (sI), cubic structure II (sII) and hexagonal structure H (sH). Each structure consists of a certain number of cavities formed by host water molecules [5]. Various other applications of gas hydrates are gas separation, gas storage and transport, natural gas recovery, storage and transport of hydrogen/natural gas, CO₂ capture and

sequestration, seawater desalination and flow assurance [6–15].

Most refrigerant gases can form gas hydrates under suitable conditions. However, their usage has been banned due to their greenhouse impact and ozone depletion potential. Carbon dioxide is a promising alternative gas that can form gas hydrate at moderate conditions [5]. Carbon dioxide forms a sI hydrate that has a dissociation enthalpy of 501–507 kJ/kg [16]. However, CO₂ hydrates cannot achieve equilibrium within the pressure ranges corresponding to temperatures used in cold storage application. Therefore, it is necessary to lower the CO₂ hydrate formation conditions which can be achieved by using promoters like quaternary ammonium/phosphonium salts.

Quaternary ammonium and phosphonium salts such as tetrabutyl ammonium halides and nitrate, tetrabutyl phosphonium halides forms semiclathrate hydrates are more suitable for cold storage application [17–22]. Semiclathrate hydrates (sc) are crystalline compounds in which, the guest molecule forms the hydrate framework along with water, apart from occupying the formed cages [23]. For example, in TBAB semiclathrate, bromine anion along with water forms the cages while the tetrabutyl ammonium cation occupies the hydrate cages [20]. The major advantage of these semiclathrate hydrates is that they can form semiclathrate hydrates at higher temperatures and atmospheric pressure. For

* Corresponding author.

E-mail address: praveen.linga@nus.edu.sg (P. Linga).

example, 40 wt % TBAB forms semiclathrate hydrate at 285.2 K at atmospheric pressure [24]. Moreover, quaternary salts are non-volatile and non-flammable solids and also are soluble in water at high concentrations. It is noted though that recent literature works have highlighted lower capacity and slow hydrate growth kinetics for semiclathrate hydrate formation systems applicable to carbon dioxide capture [25–28].

Tetrabutyl ammonium nitrate (TBANO₃) is a quaternary ammonium salt which forms semiclathrate hydrate [29]. Two types of semiclathrate hydrate phase are observed, namely: type A and type B phases with hydration numbers of 26 and 32 respectively at concentrations of 0.03 and 0.037 mol fraction [29]. TBANO₃ semiclathrate hydrate structure consists of 4 pentakaidecahedra, 16 tetrakaidecahedra and 10 pentagonal dodecahedron cages. 5 molecules of tetrabutyl ammonium cations occupy the 4 pentakaidecahedra and 16 tetrakaidecahedra, leaving the 10 pentagonal dodecahedron cages empty in type B TBANO₃ semiclathrate [29]. In Type A semiclathrate of TBAB, 6 molecules of TBA⁺ occupies 4 pentakaidecahedra, 16 tetrakaidecahedra and 4 pentagonal dodecahedron cages, leaving remaining 6 pentagonal dodecahedron cages empty [30]. These empty small cages (pentagonal dodecahedron) can be occupied by small gas molecules like CO₂, methane and hydrogen. The dissociation conditions of CO₂ + TBANO₃ semiclathrate hydrates have already been measured [31,32] at the TBANO₃ mole fraction of 3.7%. However, the phase equilibrium data for CO₂ semiclathrate in presence of TBANO₃ at mole fractions lower than 3.7% is not available in the literature, to our knowledge. Therefore, the objective of this study is to determine the semiclathrate hydrate phase equilibrium of CO₂ in the presence of various concentrations of TBANO₃. The enthalpies of dissociation calculated from the equilibrium data are also reported.

2. Experimental

2.1. Materials

Tetra-n-butyl ammonium nitrate (TBANO₃) of purity 98% supplied by Alfa Aesar was used. Carbon dioxide (CO₂) gas of purity 99.8% was supplied by Soxal Private Limited. Deionized and distilled water was used to prepare the solution.

2.2. Apparatus

The scheme of the apparatus employed in this study is depicted in Fig. 1. The hydrate phase equilibrium determination apparatus consists of a crystallizer of internal volume 142 mL (ID = 5.08 cm). The crystallizer is made up of SS 316 and the maximum operating pressure is 10 MPa. It has two windows for observation of the crystallizer contents. The temperature of the crystallizer was controlled by a cooling jacket welded to the crystallizer and an external refrigerated circulator. The temperature of the crystallizer is measured using a copper-constantan T type thermocouple of uncertainty of 0.1 K. A pressure transducer of uncertainty of 20 kPa and an analogue pressure gauge was used to measure the pressure of the crystallizer. A magnetic stirrer was used to mix the crystallizer contents. The pressure and temperature data were recorded using a data acquisition system (DAQ) coupled with a computer.

2.3. Procedure

The procedure for preparation of TBANO₃ solution of various concentrations is given in details elsewhere [26]. The isochoric pressure search method was employed to determine the semiclathrate hydrate phase equilibrium [33–39]. 53 mL of the TBANO₃ solution of required concentration was pipetted into the

crystallizer. Crystallizer was closed and a thermocouple was connected to measure the temperature of the crystallizer content. The gas supply and vent lines were connected to the crystallizer. The crystallizer was maintained at a temperature of 293.2 K using the external refrigerator. The crystallizer was flushed three times with CO₂ gas and then pressurized to required pressure. After pressurization, the crystallizer content was mixed at 500 rpm using the magnetic stirrer. Once the crystallizer pressure stabilizes, the contents were cooled to a lower temperature to form mixed semiclathrate hydrate of TBANO₃ and CO₂. The pressure and temperature stabilizes after sometime indicating the end of the semiclathrate hydrate formation. Stirring of the crystallizer contents were stopped at this point. Then, the crystallizer was heated in a step at the rate of 0.1 K/h to dissociate the formed semiclathrate hydrate. At every step, a sufficient time (~2 h) was allowed for crystallizer pressure stabilization. The crystallizer was heated up to 293.2 K in a stepwise manner. By this way the pressure and temperature profiles ($P - T$ diagram) were traced during hydrate formation and dissociation for each experimental run from which the semiclathrate dissociation point is determined. The point at which the cooling and heating curves intersect or the slope of the $P - T$ curve changes sharply was considered to be the hydrate dissociation point, and the pressure and temperature at this point are reported as the equilibrium conditions. A salient feature of our experimental facility is the ability to visually observe the presence of hydrate crystals during the heating steps. Thus we are also able to visually observe the presence of a finite number of stable hydrate crystals in the aqueous liquid at the equilibrium. The observed pressure and temperature has been found to corroborate very well with the hydrate dissociation point determined from the intersection of the cooling and heating curves in the $P - T$ curve. The expected uncertainty in hydrate dissociation pressure and temperatures are ± 0.1 K and ± 0.020 MPa respectively.

3. Thermodynamic model

Several thermodynamic models have been developed to predict the semiclathrate hydrate dissociation conditions [40–45]. Most of these models can only predict dissociation conditions of mixed semiclathrate hydrate. Paricaud model can predict both the solid – liquid phase diagram of the salt + H₂O mixtures and mixed semiclathrate hydrate dissociation condition. Recently, Paricaud et al. [46] extended the model to gas mixtures that also included TBANO₃ as the semiclathrate hydrate former. Hence, we have used the approach developed by Paricaud [45] to model the new experimental data determined for the TBANO₃ + CO₂ + H₂O system in this work. The reader is directed to the original paper for a detailed description of the model. The SAFT-VRE model is used to describe the properties of the fluid phases, and the equilibrium condition to determine the melting point of the semiclathrate hydrate is given by Ref. [45].

$$\ln(x_C \gamma_C) + \ln(x_A \gamma_A) + \nu_w \ln(x_w \gamma_w) = \sum_{i=1}^{N_{cav}} n_i \ln \left(1 - \sum_{j=1}^{N_g} Y_{ij} \right) - \frac{\Delta h^0}{RT} \left(1 - \frac{T}{T_0} \right) - \frac{\Delta v^0}{RT} (P - P_0) - \frac{\Delta g^0(T_0, P_0)}{RT_0}, \quad (1)$$

where R is ideal gas constant, T the temperature, and x_i , γ_i the mole fraction and the activity coefficient of species i , respectively. The subscripts C, A, and w denote cations, anions, and H₂O, respectively; ν_w is the hydration number in the hydrate phase. n_i is the number of cage type i per mole of salt. N_{cav} and N_g are the number of types of cavity and gas, respectively. Y_{ij} is the occupancy fraction of cavity i

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