

Phase behavior of ethane hydrate system in the presence of ammonium bromide



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ARTICLE INFO

Article history:

Received 31 July 2015
Received in revised form
6 October 2015
Accepted 7 October 2015
Available online 19 October 2015

Keywords:

Clathrate hydrate
Phase equilibria
Raman spectroscopy
Structural transition

ABSTRACT

The three-phase equilibrium curves of hydrate, aqueous, and gas phases in the ternary system of ethane (C_2H_6), ammonium bromide (NH_4Br), and water were measured at pressures up to 3 MPa and temperatures of 278.45–283.76 K. The phase equilibrium curves exhibit two trends; the curve paralleled with that of simple C_2H_6 hydrate and the one steeper than that of simple C_2H_6 hydrate. The latter implies the incorporation of NH_4Br into C_2H_6 hydrate while the former indicates the thermodynamic inhibition effect of NH_4Br . To investigate the incorporation of NH_4Br , Raman spectra of the N–H stretching vibration of NH_4^+ were analyzed. Raman spectra imply the existence of the motionally restricted NH_4^+ in the formed hydrate. Both results from the phase behavior and Raman spectra imply the formation of $C_2H_6 + NH_4Br$ semi-clathrate hydrates.

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1. Introduction

Clathrate hydrate is an inclusion compound, which has an ice-like appearance. Guest species like light hydrocarbons and noble gases construct clathrate hydrates with host water molecules. There are several kinds of hydrate cages and a couple of them are combined to form specific hydrate structures. The structure-I (sI) hydrate consists of two 5^{12} -cages (pentagonal dodecahedron, hereafter called S-cages) and six $5^{12}6^2$ -cages (M-cages) in the unit lattice. In the same manner, the structure-II (sII) hydrate is formed with sixteen S-cages and eight $5^{12}6^4$ -cages (L-cages). Crystal structures and thermodynamic stabilities of gas hydrates mainly depend on the kind of guest species [1]. The familiar guest species for the sI hydrates are methane (CH_4), carbon dioxide (CO_2), ethane (C_2H_6). The CH_4 and CO_2 molecules are able to occupy both S- and M-cages [1–5]. The C_2H_6 molecule, whose molecular size is slightly larger than the void size of S-cage, occupies only the M-cages at pressures lower than approximately 20 MPa, while high pressures enable the occupancy of the C_2H_6 molecule in S-cages as well as M-cages [6].

Besides the regular clathrate hydrates, tetraalkyl ammonium or phosphonium salts with water form semi-clathrate hydrates [7–9].

Nitrogen or phosphorus atom as well as anions forms the hydrogen-bonded frameworks with water molecules. Shimada et al. [10] have reported the isobaric phase equilibrium (temperature-composition) relations for the tetra-*n*-butyl ammonium bromide (TBAB) semi-clathrate hydrate, one of the most famous substances forming semi-clathrate hydrates. The maximum equilibrium temperature of TBAB semi-clathrate hydrate at an atmospheric pressure with the TBAB aqueous solution (mass fraction of TBAB is 0.405) is 285.15 K.

Ammonia (NH_3) molecule, only from the viewpoint of molecular size, would be able to occupy the hydrate cages because its size is similar to that of CH_4 . In fact, the previous studies [11–14] revealed that the water molecules form a dodecahedron cage (similar to S-cage) around NH_3 and ammonium ion (NH_4^+) in the gas phase. However, it had been believed that NH_3 does not form clathrate hydrates and behaves as a thermodynamic inhibitor to the clathrate hydrate formation [15,16]. Instead of clathrate hydrate formation, NH_3 hemihydrate ($2NH_3 \cdot H_2O$), NH_3 monohydrate ($NH_3 \cdot H_2O$), and NH_3 dihydrate ($NH_3 \cdot 2H_2O$) form at high pressures around 10 GPa (at room temperature) [17,18]. Shin et al. [19] reported the NH_3 clathrate hydrates (simple NH_3 hydrate, $CH_4 + NH_3$ mixed hydrate, and tetrahydrofuran + NH_3 mixed hydrate) at low temperatures and the location of the NH_3 molecules in the hydrate crystal was estimated based on the results from molecular simulation.

In the present study, we have investigated whether ammonium salts, instead of the NH_3 molecule, are possible to be enclathrated

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under the coexistence of ethane (C_2H_6) as a hydrate former. The thermodynamic stability boundary of the clathrate hydrates formed in the ternary system of $C_2H_6 +$ ammonium bromide (NH_4Br) + H_2O was measured. Not only the possibility of the enclathration of NH_4^+ (also from the Raman spectra) but the effects of NH_3 and NH_4^+ on the thermodynamic stabilities were discussed.

2. Experimental

2.1. Apparatus

The pressure-proof glass cell (Taiatsu Techno, HPG-10-1) (inner volume: 10 cm^3 , maximum working pressure: 5 MPa) was used for the phase equilibrium measurements. The experimental setup is the same as the one used previously [20,21]. The glass cell was immersed in the water bath where the temperature was controlled with the thermocontroller (Taitec, CL-80R). The equilibrium temperature was measured with the thermistor thermometer (Takara, D632, reproducibility: 0.02 K). The equilibrium pressure was measured with the pressure gauge (Valcom, VPRT, maximum uncertainty: 0.01 MPa).

2.2. Procedure

The NH_4Br (molar ratios of NH_4Br to H_2O are 1/35 ($x_{NH_4Br} = 0.028$, $w_{NH_4Br} = 0.134$) and 1/23 ($x_{NH_4Br} = 0.042$, $w_{NH_4Br} = 0.191$)) and NH_3 (molar ratios of NH_3 to H_2O are 1/35 ($x_{NH_3} = 0.028$, $w_{NH_3} = 0.026$), and 1/23 ($x_{NH_3} = 0.042$, $w_{NH_3} = 0.040$)) aqueous solutions were prepared with the electric balance (Shimadzu BL-220H, maximum uncertainty is 0.004 g), where x and w stand for the mole fraction and mass fraction, respectively. A desired volume (each is approximately 2 cm^3) of NH_3 or NH_4Br aqueous solutions was introduced into the glass cell and degassed by a freezing method. The contents were pressurized with C_2H_6 up to a desired pressure. A magnetic stirrer was moved up and down by a permanent magnet outside for agitation of the gas–liquid interface as well as the contents. The up-and-down agitating is quite important for supplying a sufficient amount of C_2H_6 in to the aqueous solution through the gas–aqueous interface. The contents were cooled and agitated to generate mixed hydrates. After the hydrate formation, the system temperature was increased by 0.1 K step every 3 h. When the disappearance of the last hydrate particle was confirmed, we determined that the system reached a three-phase equilibrium condition of $H + L_1 + G$ (H : hydrate phase, L_1 : aqueous phase, G : gas phase) with a desired composition of NH_3 or NH_4Br in the aqueous solution. After the complete dissociation of the formed hydrates, the system temperature was increased by 0.1 K step every 3 h. We confirmed the change of the slopes of the fitting curves before and after the complete dissociation.

For the Raman spectroscopy, the quenched NH_4Br aqueous solution (molar ratio of NH_4Br to H_2O was 1/35) was gained in the mortar immersed in liquid nitrogen. The powder with approximately $200\text{ }\mu\text{m}$ in diameter was loaded into the high-pressure cell and then pressurized up to 1.7 MPa with C_2H_6 . The sample was prepared at temperatures of 267 K in a temperature-controlled chamber (ESPEC, SU-241) for a couple of days. Just 1 h before the Raman analysis, the sample in the cell was moved to a cold room and kept at 253 K there. The pressure in the cell was then released and allowed to reach atmospheric pressure. Once released, the sample was kept at 77 K. A laser Raman microprobe spectrometer with a multichannel CCD detector (JASCO, NRS-1000) was used. The Diode Pumped Solid State (DPSS) laser (Cobolt, Fandango) was irradiated to the samples at atmospheric pressure and 77 K. The backscatter was taken in with same lens. The wavelength of the DPSS laser was 514.5 nm and the output power was adjusted to

100 mW. The spectral resolution of the obtained Raman spectra was approximately 1 cm^{-1} .

2.3. Materials

C_2H_6 (molar purity: 0.999) was purchased from Takachiho Trading Co., Ltd. Guaranteed research grade aqueous NH_3 solution with 28 mass% (NH_3) was obtained from Nakalai Tesque. NH_4Br (molar purity: 0.990) and distilled water were purchased from Wako Pure Chemical Industries, Ltd. All materials were used without further purification.

3. Results and discussion

The three-phase equilibrium relations of the ternary system of $C_2H_6 + NH_4Br + H_2O$ were shown in Fig. 1 and listed in Table 1. As shown in Fig. 1, two trends of phase behavior were observed in each NH_4Br mole fraction. One (closed circles and squares) is the curve (blue (in web version)) paralleled with that of the simple C_2H_6 hydrate [22,23], the other (open circles and squares) is the curve (red (in web version)) steeper than that of the simple C_2H_6 hydrate in the pressure–temperature diagram. The pressure and temperature relations of the simple C_2H_6 hydrate are correlated by the following equation:

$$\ln(p/p_0) = a + bT, \quad \text{where } p_0 = 1\text{ MPa}. \quad (1)$$

The above equation is superior to two-parameter Clausius-type equation. The constants a and b in the simple C_2H_6 hydrate system are -38.504 and 0.13793 K^{-1} (the correlation coefficient r is 0.99787), respectively. The blue curves were drawn with the same b value in Eq. (1). The drawn curves are fitted with the measured data. The values a (and r) in the NH_4Br /water molar ratios of 1/35 and 1/23 are -38.106 ($r = 0.93665$) and -37.994 ($r = 0.49159$), (where the r value is due to insufficient number of datum sets), respectively.

In the former (parallel and blue curves), NH_4Br plays a role as a

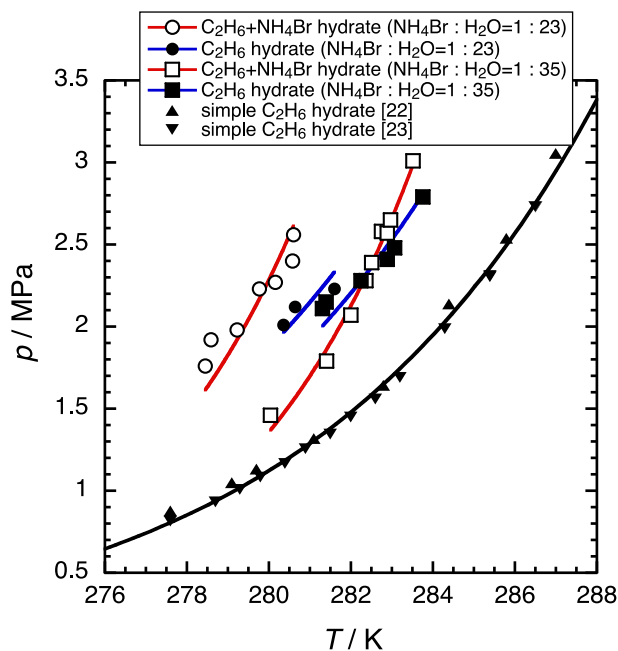


Fig. 1. Three-phase equilibrium curves of hydrate + aqueous + gas phases in the ternary system of $C_2H_6 + NH_4Br +$ water and the binary system of $C_2H_6 +$ water [22,23].

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