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Equilibrium conditions of clathrate hydrates formed from carbon dioxide and aqueous acetone solutions

Tatsuo Maekawa*

Institute for Geo-Resources and Environment, National Institute of Advanced Industrial Science and Technology (AIST), AIST Tsukuba Central 7, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8567, Japan

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ABSTRACT

Equilibrium conditions of clathrate hydrates formed from carbon dioxide and aqueous acetone solutions were experimentally measured at temperatures between 269.2 and 281.4 K and pressures up to 3.98 MPa. The acetone concentrations in solutions were investigated from 0.04 to 0.40 mass fractions. The experimental results suggested a transition in hydrate structure from structure I to another structure for acetone solutions between 0.04 and 0.12 mass fractions of acetone. The hydrate structure was suggested to be structure II which was the most stable with a 0.16 mass fraction acetone solution. For more than 0.16 mass fraction of acetone, the equilibrium conditions of the hydrate were shifted to lower temperatures as acetone concentrations increased.

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1. Introduction

Clathrate hydrates are solid crystalline compounds formed from water and relatively small guest molecules. Within the hydrate lattice, water molecules form a hydrogen-bonded cage-like structure encapsulating the guest molecules. The hydrate structures have been classified into structure I, structure II and structure H by the difference in cage sizes and shapes [1]. In general, small gas molecules such as methane, ethane and carbon dioxide can form a structure I hydrate as a single guest, whereas propane can form a structure II hydrate. Organic compounds such as tetrahydrofuran and acetone can also form structure II hydrates with water. A structure H hydrate can be formed from larger molecules such as methylcyclohexane and another guest gas such as methane.

Clathrate hydrates have been of interest to the oil and gas industry because their formation can result in the blockage of pipelines and processing facilities. Experimental data of clathrate hydrates have been extensively presented over many years, especially for natural gases containing methane and carbon dioxide. It was found from them that adding some electrolytes and alcohols such as methanol can inhibit the hydrate formation by shifting the formation conditions to higher pressure and lower temperature [2,3]. Recently, some technological applications using clathrate hydrate formation have been proposed such as the storage and transportation of natural gases [4,5]. For the applications, hydrate promoters can be used which allow hydrate to form easily at milder conditions. Tetrahydrofuran, one of the hydrate promoters, have been also expected for some other possibilities such as hydrogen storage in hydrate [6] and recovery of carbon dioxide from flue gas [7].

It has been known that acetone also has a hydrate promoting effect. Acetone can form structure II hydrate with water as a single guest and the phase diagram of the acetone + water system was considered in Dyadin et al. [8]. According to Ng and Robinson [9] investigating methane hydrate formation with aqueous acetone solutions, acetone can act as a methane hydrate promoter at relatively low acetone concentration in solution. They also reported an inhibiting effect of acetone on methane hydrate formation at high acetone concentrations of 0.75 and 0.90 mass fractions. Javanmardi et al. [10] showed that acetone suppresses R22 ($CHClF_2$) hydrate formation for all the investigated acetone concentrations of 0.02, 0.04 and 0.06 mole fractions. Imai et al. [11] investigated the effects of acetone on clathrate hydrate formation of difluoromethane or krypton using an acetone solution which had 17 mole ratio of water to acetone. They found that the hydrate equilibrium temperatures of difluoromethane with the acetone solution were lower that those with pure water at the same pressure above 0.2 MPa, whereas those of krypton with the acetone solution were substantially higher than those with pure water throughout the investigated pressure. The equilibrium conditions of clathrate hydrates formed from propane and aqueous acetone solutions were experimentally measured [12], indicating that acetone has an inhibiting effect on propane

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* Tel.: +81 29 861 3720; fax: +81 29 861 3717.
E-mail address: tatsu-maekawa@aist.go.jp

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hydrate similar to the effect on R22 hydrates. Considering the results mentioned above, the inhibiting or promoting effect of acetone on clathrate hydrate formation depends on its concentration in solution and species of guest gas molecules. Few experimental data of clathrate hydrate formed from carbon dioxide and aqueous acetone solution have been presented except for those obtained in Seo et al. [13] where a 0.03 mole fraction acetone solution was examined. In the present study, equilibrium conditions of the clathrate hydrates formed from carbon dioxide and different concentrations of aqueous acetone solutions were experimentally measured. The acetone concentrations of the solutions were investigated between 0.04 and 0.40 mass fractions.

2. Experimental

2.1. Materials

Deionized water was distilled in the laboratory before use. Carbon dioxide of research grade purity was supplied by Showa Tansan Co. Ltd. The acetone used in the present study was supplied by Wako Pure Chemical Industries, Ltd. The minimum purity is 0.998 on a mass basis. Appropriate amounts of acetone and distilled water were weighed on an electronic balance with a resolution of 0.01 g and mixed thoroughly at room temperature. The uncertainties in composition of solutions are estimated to be less than ±0.0004 on a mass fraction basis.

2.2. Experimental apparatus

The experimental apparatus used in the present study is the same as that used in previous studies [14,15]. The main part of the apparatus is a cylindrical stainless-steel cell with a volume of approximately 1000 cm^3. The cell is immersed in a glycol–water bath of which the temperature is controlled by an external heater and refrigeration unit. The cell is equipped with a mixer to agitate the solution and hydrate crystals inside the cell. The temperature and pressure inside the cell are measured with a platinum resistance thermometer and a semi-conductor pressure transducer calibrated by a precise Bourdon tube gauge, respectively. The estimated uncertainties of temperature and pressure measurements are ±0.2 K and ±0.04 MPa, respectively. The fluctuation in temperature controlled by the heater and refrigeration unit was hardly observed.

2.3. Experimental procedures

Equilibrium conditions of clathrate hydrate formation were measured using the isochoric procedure described previously [14,15]. In each experimental run, approximately 700 cm^3 of aqueous acetone solution was charged into the cell. After sealing the lid, the cell was immersed in the temperature-controlled bath. The cell was repeatedly flushed with carbon dioxide supplied from a high-pressure cylinder, and carbon dioxide was then introduced into the cell until the desired pressure was reached. The valve of the cell was closed and the temperature was then lowered to form hydrate with stirring. After hydrate formation was detected by a rapid decrease in pressure due to encapsulation of carbon dioxide in the hydrate, the temperature was raised to a temperature slightly lower than the predicted equilibrium temperature. Subsequently, the temperature was raised in steps of 0.1 K to dissociate the hydrate. At every step, the temperature was kept constant for 4 h to achieve a steady equilibrium state. While the temperature was raised in the presence of hydrate, a marked increase in pressure was observed at each step due to partial dissociation of the hydrate. In contrast, once all the hydrate was dissociated, only a small pressure increase was observed due to thermal expansion and fluid phase equilibria. The point at which the slope of measured pressure to temperature abruptly changed is considered to be the hydrate dissociation point. Therefore, the hydrate equilibrium conditions were determined by measuring the pressure and temperature of the hydrate dissociation point. To obtain another equilibrium condition, the initial pressure was changed and the procedure was repeated.

The phase equilibria of vapor–water-rich liquid–condensed carbon dioxide-rich liquid (VLL) were also measured in the present study. The measurements were performed without clathrate hydrate formation at a constant temperature. The carbon dioxide was introduced into the cell up to the pressure below the predicted VLL equilibria. Subsequently, a small amount of carbon dioxide was added. Unless the condensed carbon dioxide-rich liquid phase existed, the pressure was raised by about 0.05 MPa. On the other hand, the increase in pressure was hardly observed while condensed carbon dioxide-rich liquid phase formed. The equilibrium was obtained where the pressure was hardly raised during stepwise addition of carbon dioxide. The data obtained in conditions of possible hydrate formation indicate metastable VLL equilibrium conditions without hydrate.

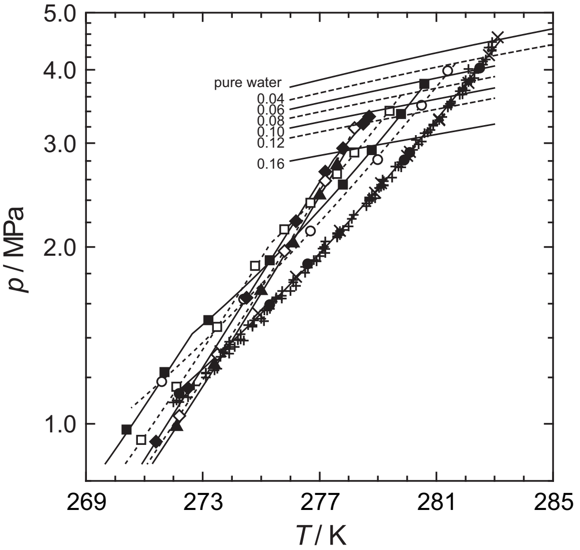

Fig. 1. Equilibrium conditions of clathrate hydrates formed from carbon dioxide and pure water ((●) the present study, (+) the previous data [1], (×) the previous data [15]) and aqueous acetone solutions between 0.04 and 0.16 mass fractions: (○) $w = 0.04$, (■) $w = 0.06$, (□) $w = 0.08$, (♦) $w = 0.10$, (◊) $w = 0.12$, (▲) $w = 0.16$. Lateral lines indicate VLL equilibria obtained from set of the measured data for each acetone solution. Numerical values besides the lines are the mass fractions of acetone in solution.

3. Results and discussion

Equilibrium conditions of clathrate hydrates obtained in the present study are tabulated in Table 1. The data are also graphically shown in Figs. 1 and 2 using semi-logarithmic plots with a logarithmic scale on the vertical axis indicating pressure. The experimental data for pure water and acetone solutions between 0.04 and 0.16 mass fractions are shown in Fig. 1 and those for acetone solutions between 0.16 and 0.40 mass fractions are shown in Fig. 2. The measured VLL equilibria of the carbon dioxide–acetone–water system are tabulated in Table 2 and also shown in Fig. 3. In the figures, the VLL equilibria are also indicated as a line fitted to the set of the measured data for each acetone solution using a least-square method.

As seen in Fig. 1, the equilibrium conditions of carbon dioxide hydrates with pure water are consistence with the corresponding

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