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Solubility measurements for the $CH_4 + CO_2 + H_2O$ system under hydrate–liquid–vapor equilibrium

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ABSTRACT

Phase equilibria for the $CH_4 + CO_2 + H_2O$ system have been investigated in the past, but mole fraction of methane and carbon dioxide in the bulk liquid phase has not been measured under hydrate–liquid–vapor equilibrium. Equilibrium liquid composition is very important as it defines the driving force for hydrate growth. This study presents the solubility of methane and carbon dioxide under H–Lw–V equilibrium. Emphasis is made on the effect of pressure along the respective isotherms on the equilibrium mole fraction of the individual hydrate formers in the liquid.

1. Introduction

Gas hydrates, or clathrate hydrates, are non-stoichiometric crystalline compounds in which guest molecules of suitable size and shape are trapped inside a network of hydrogen-bonded water molecules. The water network is stabilized by weak van der Waals forces between the host and the guest molecules. Clathrate hydrates occur naturally in permafrost regions and in sub-sea sediment where existing pressures and temperatures allow for thermodynamic stability of the hydrate [1]. Hydrates crystals were discovered in the 1800s and were investigated strictly from an academic point of view until a major discovery in the 1930s [2]. It was then recognized, that plugging of natural gas pipelines was due to the formation of natural gas hydrates and not to ice [3]. The latter transformed hydrate research from a small academic field into a highly applied field with wide interest particularly to the oil and gas industry.

Various other motives for hydrate research have surfaced more recently. Hydrates of natural gas have been discovered *in situ* [4]. Most of these natural gas hydrates are found in the ocean bottom; however, there is a considerable amount of hydrates found in permafrost regions [5]. Conservative estimates suggest that the energy stored in the form of hydrates exceeds all other hydrocarbon sources combined [6]. In addition to being a potentially vast energy source for the future, the enormous quantities of methane stored as hydrates also pose an environmental concern due to the high global warming potential of methane [7]. Hydrates have also been suggested as an economically advantageous alternative to liquefied natural gas (LNG) for transportation and storage of gas [8]. Carbon dioxide is also an important hydrate former both because of its negative greenhouse properties [7] as well as its presence as a contaminant in natural gas [9]. The use of hydrate technology to sequester CO_2 from mixed streams containing either N_2/CO_2, H_2/CO_2 or CH_4/CO_2 mixtures is currently being explored [10,11].

Based on the combination and ratio of hydrate formers the crystalline and thermodynamic properties can vary significantly from that of hydrate formed from pure guests [1]. By taking advantage of these particular mixture properties it has been experimentally proven that it is possible to selectively replace enclathrated methane using carbon dioxide gas under the appropriate thermodynamic conditions [12]. More recently it has been shown that gas hydrates can be used to reduce the carbon dioxide content in methane/carbon dioxide mixtures containing 25% CO_2[11].

A better understanding of mixed hydrate systems phase equilibria is required in order to exploit the potential applications of hydrate formation in the presence of gas mixtures. Previously, bulk liquid phase solubility experiments have been performed for pure methane and carbon dioxide in water in presence of hydrates [13,14]. Phase equilibria for the system $CH_4 + CO_2 + H_2O$ have been investigated in the past [12,15–20], but to the best of our

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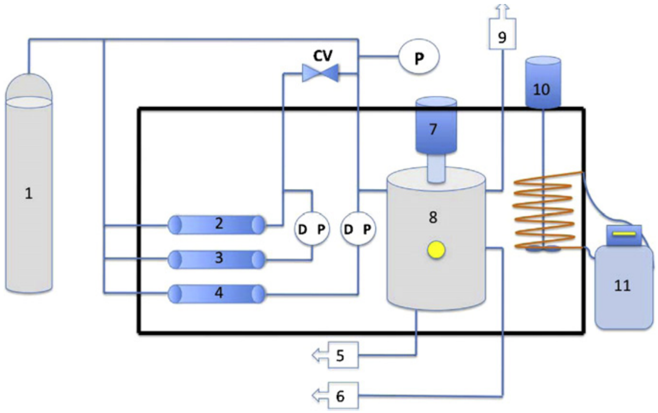

Fig. 1. Schematic of the apparatus: (1) gas source, (2) reservoir, (3) reservoir bias, (4) crystallizer bias, (5) liquid port (low), (6) liquid port (high), (7) magnetic stirrer, (8) crystallizer, (9) gas port, (10) stirrer, (11) chiller; CV: control valve, P: pressure transducer, DP: differential pressure transducer.

knowledge the equilibrium mole fraction of methane and carbon dioxide in the bulk liquid phase has not been measured under hydrate–liquid–vapor equilibrium for this mixed system. Equilibrium liquid composition is very important as it defines the driving force for hydrate growth [21,22]. The present study addresses this gap in the understanding of the phase equilibrium for the system $CH_4 + CO_2 + H_2O$ by presenting the solubility of methane and carbon dioxide under H–Lw–V equilibrium. Emphasis is made on the effect of pressure along the respective isotherms on the equilibrium mole fraction of the individual hydrate formers in the liquid.

2. Experimental apparatus

A simplified diagram of the setup is illustrated in Fig. 1. The crystallizer is made of 316 stainless steel with a pressure rating of 20 MPa. It is equipped with a MM-D06 magnetic stirrer from Pressure Product Industries and has two polycarbonate windows to allow for visual inspections. The crystallizer is connected to a reservoir using a Baumann 51000 control valve which makes it possible to maintain constant pressure during liquid sampling. Reactor and reservoir biases are also in place to increase the accuracy of the pressure readings in the system. The entire system is immersed in a temperature controlled bath consisting of a 20% ethylene-glycol/water mixture. The pressure is monitored using Rosemount pressure transducers configured to a span of 0–14 MPa and differential pressure transducers configured to a span of 0–2 MPa, with an accuracy of ±0.065% of the given span. The system temperatures are monitored using high accuracy (±0.1 K) RTD probes from Omega. All readings were automatically recorded using a National Instruments data acquisition system. The liquid sample ports are equipped with a Norman 4200 in-line filters which retain particles greater than 200 nm in diameter. The filters prevent the collection of unwanted hydrate particles with the liquid samples. A digital gasometer from Chandler Engineering is used to measure the amount of gas flashing out of the liquid when the sample is left to equilibrate at room temperature and atmospheric pressure. A gas chromatograph (Varian CP-3800) equipped with a sampling valve and a TCD detector is used to obtain vapor phase compositions.

3. Experimental procedure

Hydrate–liquid–vapor (H–Lw–V) solubility experiments for the system $CH_4 + CO_2 + H_2O$ were performed using previously reported knowledge of multicomponent gas hydrate phase equilibria [20,23] combined with a flash technique used for solubility measurements applied in the past to single hydrate formers systems [13,14]. To begin an experiment, the crystallizer was filled with 300 mL of distilled deionized water. The gas phase was then flushed three times using a high purity gas mixture of CH_4 + CO_2 (MEGS) by pressurizing the crystallizer to 1000 kPa and then purging the gas phase to remove any air left in the reactor. The system was then pressurized with the same mixture of CH_4 + CO_2 to allow saturation and hydrate formation at constant temperature. Subsequently, the system was left to equilibrate while the temperature was kept constant. Gas was not supplied to the system during the equilibrating stage of the experiment. When the pressure reached a constant value (unchanged for 5 h) a vapor-phase sample and a hydrate-free, liquid sample were collected into separate, evacuated sample bombs for further analysis. The composition of the vapor phase was analyzed directly in the gas chromatograph, and the resulting mole fraction was compared with the corresponding literature values [12,17–20] in order to guarantee the system had reached equilibrium. The liquid samples were flashed prior to further analysis. The latter involved bringing the liquid sample bomb to room temperature and atmospheric pressure by expansion of the sample into the gasometer. When gas stopped evolving from the liquid, the sample bomb was heated to 353 K to ensure the remaining gas present in the liquid phase flowed into the gasometer. The sample bomb was then disconnected from the gasometer, and the remaining gas in the gasometer chamber was allowed to equilibrate to room temperature.

The number of moles of CH_4 and CO_2 in the gasometer is given by Eq. (1):

$$n_i^G = y_i^G (p - p_{H_2O}) \frac{V}{ZRT} \tag{1}$$

where p, p_{H_2O}, V, y_i^G, R, T, Z are atmospheric pressure, vapor pressure of water at room temperature, volume of the vapor phase in the gasometer, mole fraction of the respective component in the vapor phase, universal gas constant, room temperature, and the compressibility factor for the given gas mixture. The compressibility factors were obtained from the Trebble–Bishnoi equation of state [24–26]. By knowing the weight of the sample bomb, as well as by analyzing the vapor evolved from the liquid phase sample, the mole fraction of the respective hydrate formers could be calculated. x_i^{EQ} represents the equilibrium mole fraction of component i in the liquid phase of a gas mixture at the experimental temperature and pressure as given by Eq. (2) where n_i^G is the number of moles of component i in the liquid sample and n_{TOT} is the total number of moles in the liquid sample.

$$x_i^{EQ} = \frac{n_i^G}{n_{TOT}} \tag{2}$$

Using the method described above to determine the equilibrium conditions, it was estimated that the standard uncertainties were as follows: for temperature $u_T = 0.1$ K, for pressure $u_p = 0.015$ MPa, for the vapor-phase mole fraction of CO_2 $u_{yCO_2} = 0.02$, for the solubility of methane $u_{xCH_4} = 0.000040$, and for solubility of carbon dioxide $u_{xCO_2} = 0.00027$. With a coverage factor of $k = 2$ and assuming the corresponding standard uncertainty had a normal distribution, each expanded uncertainty was estimated to be $U_T = 0.2$ K, $U_p = 0.03$ MPa, $U_{yCO_2} = 0.04$, $U_{xCH_4} = 0.000080$, and $U_{xCO_2} = 0.00054$.

4. Results and discussion

Solubility experiments were conducted under hydrate–liquid–vapor equilibrium. Experimental conditions ranged from 274 to 280 K and 1.4–5 MPa. The data are tabulated in Table 1 and are also plotted in Fig. 3 for methane and Fig. 4 for carbon dioxide, respectively. Mixtures of carbon dioxide and