Fluid Phase Equilibria 367 (2014) 95–102

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Phase equilibrium of semiclathrate hydrates of methane in aqueous solutions of tetra-n-butyl ammonium bromide (TBAB) and TBAB–NaCl

Jitendra S. Sangwai[a,*], Lothar Oellrich[b]

[a] Petroleum Engineering Program, Department of Ocean Engineering, Indian Institute of Technology Madras, Chennai 600036, India
[b] Institut für Technische Thermodynamik und Kältetechnik, Karlsruhe Institute of Technology, Karlsruhe, Germany

ARTICLE INFO

Article history:
Received 12 September 2013
Received in revised form 21 January 2014
Accepted 26 January 2014
Available online 3 February 2014

Keywords:
Gas hydrate
Methane
Semiclathrate hydrate
Sodium chloride
Tetra-n-butyl ammonium bromide

ABSTRACT

Phase equilibria of semiclathrate hydrates are important for their successful engineering applications due to more favorable process conditions compared to classical gas hydrate systems. Though sufficient information on the phase equilibria of semiclathrate hydrates of methane (CH_4) in tetra-n-butyl ammonium bromide (TBAB) seems to be available, there are pronounced disagreements on the phase equilibrium data, particularly for 0.05 and 0.20 mass fraction (w) of TBAB. In this work, experimental studies are carried out to generate the equilibrium pressure (P) and temperature (T) for hydrates and semiclathrate hydrates of CH_4 in an aqueous solution containing $w_{TBAB} = 0.05$ and 0.20 at P and T range of 1.02–13.73 MPa and 281.63–294.54 K, respectively. This study tries to clarify the discrepancy of published data in the literature and their reliability. Additionally, we present interesting insights into the phase behavior of semiclathrate hydrate of methane in TBAB based on the formation and dissociation curves observed in the experiments. It is *observed* that there existed two equilibrium points during the dissociation of semiclathrate hydrates of methane in TBAB; one closely corresponds to the pure methane hydrate phase stability curve and the second one to the semiclathrate hydrate system of methane. In addition phase equilibrium data is generated for the quaternary system of $CH_4 + TBAB + H_2O + NaCl$ for $w_{NaCl} = 0.03$ and 0.10 and $w_{TBAB} = 0.05$ and 0.20 in an aqueous solution at a P and T range of 1.65–20.71 MPa and 281.19–296.38 K, respectively. This is not yet available in the open literature. It is observed that NaCl inhibits the semiclathrate hydrate formation of CH_4 in TBAB for $w_{NaCl} = 0.03$ and 0.10 in $w_{TBAB} = 0.20$ in the system. However, a promotion effect is observed for $w_{NaCl} = 0.03$ in $w_{TBAB} = 0.05$. This study calls for more detailed investigations on the effect of salts on semiclathrate hydrate systems, which may find potential use in engineering applications.

1. Introduction

Gas hydrates, generally referred to as clathrate hydrates, are ice like structures in which guest gas molecules, such as methane, carbon dioxide, etc., are trapped inside cages formed by the host water molecules. These cages are built by host water molecules by hydrogen bonding. Gas hydrates do form at condition of high pressure and temperatures above 273 K and show the formation of different structures, such as, structures I, II and H depending upon the formation conditions of temperature, T, and pressure, P, and the type of entrapped guest molecules inside the water cages [1]. Gas hydrates also offers a potential solution for natural gas storage and transportation worldwide and as an alternative to LPG and CNG [2,3]. Several additives (promoters) are being investigated for safer applications of hydrates for engineering applications. Additives which promote the formation of gas hydrates by shifting the phase equilibrium curve toward lower pressure and higher temperature condition are called thermodynamic *promoters*, those which shift the phase equilibrium curves toward higher pressure and lower temperature conditions are called thermodynamic *inhibitors*. One of several additives which thermodynamically promote the formation is the class of tetra-n-alkyl ammonium halides (bromide, TBAB; chloride, TBAC; or fluoride, TBAF). These are types of phase transfer catalysts, which, when added in water form semiclathrate structures at a pressure much lower than that required for gas hydrates at a given temperature [4]. The structure of semiclathrate compound is not exactly similar to gas hydrates but share many of the physical and structural properties as that of clathrate hydrates. Unlike clathrate hydrates where guest gas molecules reside in the cages formed by the host water molecules, in semiclathrate hydrates, the halide ion forms the cages along with water molecules and the tetra-n-butyl ammonium cation resides in the larger cages while the smaller cages are accommodated by small

---

[*] Corresponding author. Tel.: +91 44 2257 4825; fax: +91 44 2257 4802.
E-mail addresses: jitendrasangwai@iitm.ac.in, jitendrasangwai@yahoo.com (J.S. Sangwai).

0378-3812/$ – see front matter
http://dx.doi.org/10.1016/j.fluid.2014.01.036

guest gas molecules such as methane or CO_2 [5,6]. Like gas hydrates, semiclathrate hydrates are also capable of selectively trapping large volumes of gases within a molecular framework of water molecules [7].

Phase equilibrium data of the semiclathrate hydrates are important for their successful engineering applications due to more favorable process conditions compared to gas hydrate systems. In recent years phase equilibria in TBAB semiclathrate hydrate systems for various gaseous systems have been investigated by several researchers. Arjmandi et al. [4] conducted experiments to generate equilibrium data for H_2, CH_4, N_2, CO_2 and natural gas in semiclathrate hydrates of TBAB. They observed that the semiclathrate hydrates of TBAB are more stable than pure gas hydrate. Hashimoto et al. [8] measured three phase equilibrium data for semiclathrate hydrates of hydrogen–TBAB aqueous system up to 10 MPa. They observed that the three phase equilibrium curve for various concentrations of TBAB at high pressures converge to the pure TBAB aqueous solution having the same concentration. Li et al. [9] generated phase equilibrium information for the hydrates of mixture of $CO_2 + H_2$ in TBAB aqueous solution. They observed that the presence of TBAB helps to reduce the hydrate formation pressure at a given temperature compared to pure hydrates. Li et al. [10] studied the phase equilibria for CO_2 in the presence of tetra-n-butyl ammonium halide. It is observed that all the promoters such as, TBAB, TBAC, and TBAF can enlarge the hydrate stability zone which is directly proportional to their concentration in the aqueous systems. Mohammadi et al. [11] studied the phase equilibrium of CO_2, N_2, CH_4 and H_2 gases in TBAB aqueous system. They observed that exceeding a particular stiochiometric ratio, the TBAB addition results in inhibition of semiclathrate hydrate. A brief summary of the studies related to phase equilibrium of semiclathrate hydrate system in TBAB aqueous solution with various gases as guest molecule is presented in Table 1. Though sufficient information seems to be available on the phase equilibria of semiclathrate hydrates of methane in TBAB, there are pronounced disagreements and confusion on the reliability [11,19], particularly for 0.05 and 0.20 mass fraction (w) of TBAB.

Salts/electrolytes such as sodium chloride (NaCl), calcium chloride ($CaCl_2$), potassium chloride (KCl), magnesium chloride ($MgCl_2$), etc., inhibit the hydrate formation by lowering the activity of water in liquid phase. Naturally occurring water typically contains dissolved salts whose effect on the semiclathrate hydrate forms an important precursor for practical applications, such as gas storage and transportation. However, hitherto existing studies involving their effect on the phase behavior of the semiclathrate hydration system are rare [35,36]. Additionally, models for the simple semiclathrate hydrate system containing different gases as guest molecules have been developed recently [37–40] however in the absence of data relating their behavior in complex environment, such as presence of salts. This needs further development on experimental and modeling investigations on phase behavior of these systems for complex environments for successful practical application [1,3]. Indeed, TBAB shows promising economical alternative to gas hydrate and also to other promoters, like, tetrahydrofuran (THF), which shows greater environmental and economic concern for a possible practical application [41].

In our efforts to study the reliability of existing phase equilibrium data for few mass fractions of TBAB, viz., $w = 0.05$ and 0.20, we observed interesting insights into the occurring phase behavior of semiclathrate hydrate of methane in TBAB based on the formation and dissociation curves which are presented herewith, along with the data on phase equilibrium of the same. In addition, the effect of NaCl on the phase behavior of semiclathrate hydrate of methane in TBAB is studied for $w_{\mathrm{NaCl}} = 0.03$ and 0.10 for $w_{\mathrm{TBAB}} = 0.05$ and 0.20 mass fraction in an aqueous solution. The equilibrium pressure and temperature data are presented for all studied combinations and for the effect of NaCl on the phase equilibria of semiclathrate hydrates of methane, which will help to develop robust phase behavior models for efficient engineering applications.

2. Experimental details

2.1. Experimental set-up and materials

A 1 l autoclave is used to determine the four phases; hydrate–semiclathrate hydrate–liquid–gas (H–SCH–L–V) equilibrium condition of the semiclathrate hydrate system and is shown in Fig. 1. It is to be noted here that semiclathrate hydrate and (classical) hydrate of methane are two distinct phases. The measurement of the hydrate/semiclathrate hydrate phase stability can be carried out using one of the methods mentioned in the literature, such as, visual, isobaric, and isochoric [42–48]. In this work the isochoric method is used [45–47]. An aqueous phase amounts about half of the reactor and the rest is occupied by the gas (methane) at a desired pressure. The reactor is stated for a maximum working pressure of 25 MPa. The temperature control of the reactor is achieved by circulating water at a desired temperature from the Julabo® (model F-32) water bath to within ±0.05 K. The temperatures of the mantle of the reactor and that of the liquid and gas phase are measured using Platinum-100 (Pt-100) sensor with an uncertainty of ±0.1 K. The pressure of the hydrate cell is measured using a Rosemount™ Pressure Transducer (Model 3051 TA, 0–25 MPa) with an uncertainty of ±0.001 MPa of the measured pressure span.

The methane gas (0.9995 mass fraction purity) used in this study is supplied by Air Liquide. Deionized water is used throughout the study to form the solutions of TBAB. TBAB with 0.50 mass fraction aqueous solution is supplied by Sigma Aldrich®. NaCl is supplied by Carl Roth® GmbH with a stated purity of 0.999 mass fraction. The methane gas and chemicals are used as they were received from the manufacturer. Deionized water is added to the 0.50 mass fraction solution of TBAB to prepare the desired concentration of TBAB in water (for this study, $w_{\mathrm{TBAB}} = 0.05$ and 0.20). The mass fractions of NaCl used in this study are, $w_{\mathrm{NaCl}} = 0.03$ and 0.10. A Mettler-Toledo balance (model PM 6100) with double digit precision and with a mass uncertainty of ±0.0001 g is used to prepare the solutions. The details of the chemicals used for this study are given in Table 2.

2.2. Experimental procedure

Before the start of an experiment, the reactor is cleaned twice with deionized water (conductivity < 1 μS/cm) followed by the application of vacuum to remove traces of water from the reactor. For the actual experiment, a solution of the required chemicals is filled (500 ml) into the reactor. The solution is then degassed twice using pressurized methane (at about 0.5 MPa) to remove any traces of dissolved air. The reactor is then charged with methane gas at a desired pressure. The content of the reactor is stirred vigorously using a high performance magnetic stirrer at about 800 RPM. This speed of the stirrer has been observed to be optimum to predict the correct equilibrium point of the system [45–47]. At the start of the experiment, the system was allowed to come in thermodynamic equilibrium outside the gas hydrate phase. This is then followed by fast cooling of the mixture at the rate of about 10 K/h. The system's pressure and the temperature are measured online using LabView® and recorded with sampling time of 20 s and are plotted on a P–T (pressure and temperature isochors) diagram. The sudden drop in the pressure of the system at one point on the isochors represents the onset of the formation of gas hydrate [45–47]. After the onset of the gas hydrate formation, cooling of the reaction mass is continued till the pressure decreases by about 0.8–1 MPa