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Solubility measurement of carbon dioxide in water in the presence of gas hydrate

M.J. Najafi, V. Mohebbi*

Ahwaz Petroleum Faculty, Petroleum University of Technology (PUT), Ahwaz, Iran

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ABSTRACT

In order to use the fugacity or solubility as the driving force during hydrate formation, we need to measure the mole fraction of hydrate former gases in the liquid phase. In this study, the mole of CO_2 in water was measured and reported. The isobaric experiments were conducted at temperatures between 275 and 281 K and different degrees of super saturation, which is the ratio of the experimental pressure to the hydrate equilibrium pressure at the same temperature. Also the influence of temperature and pressure on the solubility of gas in liquid in the presence of hydrate has been investigated. Results show that solubility of CO_2 in water (during hydrate formation) is relatively close to the solubility of CO_2 at the same temperature but corresponding equilibrium pressure. In addition, the solubility and (consequently) the fugacity of the aqueous phase are constant during hydrate growth stage.

1. Introduction

Gas hydrates are nonstoichiometric crystal compounds in which at appropriate temperature and pressure, and with a sufficient amount of water, molecules with appropriate size and shape are trapped in a network of weak hydrogen bonds (Sloan and Koh, 2007). Molecular carbon dioxides can reside in these networks due to these features, and this leads to the formation of hydrates.

Since a couple of decades ago, the discussion of hydrates had focused on the prevention of their formation in pipe lines. However, today, hydrates can be used in processes such as gas purification (Ho et al., 2013; Surovtseva et al., 2011)_ENREF_1, water desalination (Javanmardi and Moshfeghian, 2003; Park et al., 2011), gas storage and transportation (Adeyemo et al., 2010; Kim et al., 2010; Kumar et al., 2006; Yuan et al., 2012). In addition, disposal and decomposition of the carbon dioxide gas hydrate which may enhance global warming is under consideration now (Babu et al., 2013).

Gas hydrates can be studied with regard to both thermodynamics and kinetics. Numerous studies have been done since 1934 with regard to thermodynamics and kinetics (Hammerschmidt, 1934). Hydrates kinetics are very important in the investigation of gas hydrates, modeling, prediction of forming, growth, and decay conditions. Better recognition of the hydrate kinetics can be obtained by investigation of gas solubility (Servio and Englezos, 2001).

The first fundamental question in the modeling of hydrate kinetic is the definition of the driving force. Various opinions have been stated with regard to reality of driving force and hydrate crystallization. A fugacity driving force was first applied by Englezos et al. (1987a,b) and was defined as the difference between the fugacity of liquid bulk and surface of particles. Kashchiev and Firoozabadi (2002) investigated the super saturation state in growth processing and selected chemical potential to explain their model; While Christiansen and Sloan (1995) proposed total Gibbs energy as the driving force. Arjmandi et al. (2005) and Vysniauskas and Bishnoi (1983, 1985) proposed degree of subcooling as the driving force. Finally, Skovborg and Rasmussen (1994) selected concentration to explain their model.

Based on Henry's law, fugacity is proportional to concentration (of insoluble gases) which means that the fugacity can be estimated using solubility. Few studies have been done regarding the time of growth of hydrate processing. Hashemi et al. (2007) used Clarke and Bishnoi (2004) findings and stated that liquid bulk concentration of carbon dioxide does not change radically after the growth process has started. They argued that the gas which is in water and in super-saturation state is used to form hydrate and the system reaches saturation and equilibrium while it is reaching equilibrium (Hashemi et al., 2007).

Various authors explained the amount and trend of carbon dioxide dissolution in water while hydrates are formed at equilibrium. Yang et al. (2000); Someya et al. (2005); and Servio and

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* Corresponding author. Tel.: +98 6115550868.
E-mail address: mohebbi@put.ac.ir (V. Mohebbi).

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Englezos (2001) stated that dissolution increases at the hydrate formation region by increasing temperature. Teng et al. (1997) predicted the reverse process. Ohmura and Mori (1999) stated that the experiments of Teng and Yamasaki were conducted in metastable region and absence of hydrate. Yang et al. (2000); Someya et al. (2005); and Servio and Englezos (2001) stated that pressure does not have a strong impact on solubility.

In this study, we measured and investigated carbon dioxide dissolution in water at various temperatures and pressures during hydrate formation. There are several studies in the literature that consider the fugacity (or concentration) derivative of hydrate former in the aqueous phase with respect to time in their modeling (Englezos et al., 1987a, 1987b; Chun and Lee, 1996; Mahendra et al., 1997; Bergeron and Servio, 2008). We show that the solubility (concentration) does not change during the hydrate growth through time. In other words, we measured that the gas concentration change with time in the liquid phase, can be ignored in modeling. This fact can considerably reduce calculations in hydrate kinetic study. In addition, the solubility trend with respect to temperature and pressure has been investigated in this work.

2. Experimental apparatus and procedure

2.1. Apparatus

Fig. 1 shows a schematic diagram of the apparatus used for CO_2 solubility measurement. A stainless steel 316 cell with a volume of 271 cm^3 and a maximum working pressure of 20 MPa is the main part of the present setup.

A mechanical stirring was used in order to increase gas/water contact and enhance hydrate formation (Ngan and Englezos, 1996). Two adjustable impellers which connected to the axle were used for mixing of the mixture. The top impeller rotation prevents accumulation of hydrate crystals at the interface. Mixing of the cell mixture is accomplished using a magnetic bar. All the experiments were carried out at 270 rpm.

The crystallizer (cell) and the auxiliary cell ware all immersed in an insulated bath consisting of ethylene glycol/water mixture. The temperature is regulated by an external refrigerator and a heater (±0.1 K). A mixer was used to maintain uniform mixture in the glycol–water bath. A PC was used for direct data acquisition of the experimental pressures and temperatures. The experimental pressure and temperature data are saved and displayed simultaneously in a PC.

Two temperature indicators (PT-100) at two different levels of the bath indicate the temperatures of system (±0.1 K). The cell pressure has been displayed in the data acquisition system by a Sensys pressure transmitter with the accuracy of 10 kPa. An Ashcroft digital pressure gauge has been used to show the cell pressure (±0.5% span accuracy).

2.2. Procedure

Prior to any experiment, the cell was pressurized with carbon dioxide and evacuated with a Speedivac vacuum pump three times. Then, 125 ml of double distilled water with conductivity less than 0.1 μS/m was injected to the cell. The cell was pressurized with carbon dioxide up to below the hydrate formation pressure, and it was let to be cooled to the desired temperature.

To achieve the isothermal condition, high purified CO_2 is injected to the hydrate cell after 30 min to maintain the desired pressure and to ensure constant pressure cell throughout the experiment (P_{exp}). The mixer and data-acquisition are started after two temperatures of the bath became constant (T_{exp}). As this study is concentrated on the solubility measurement after hydrate formation, it is essential to identify the hydrate growth step. The hydrate growth stage can be identified as the cell pressure starts to decrease. The solubility measurement was carried out at several times after hydrate growth.

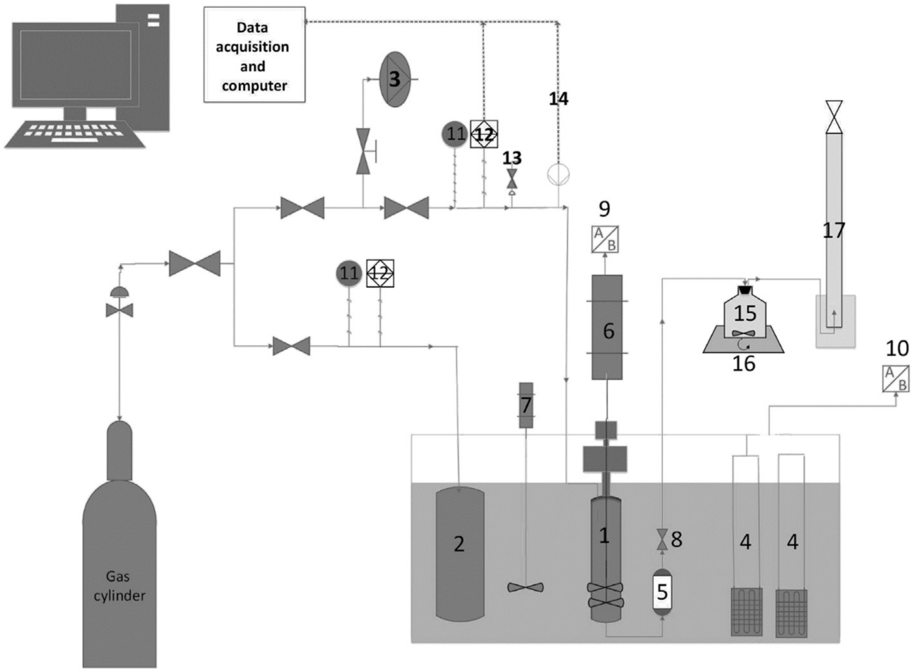

Fig. 1. Schematic of the experimental set-up: (1) the main cell which is briefly called cell; (2) auxiliary cell; (3) vacuum pump; (4) heater and refrigerator for control temperature of system; (5) micro filter (metering valve); (6) electromotor; (7) mixer; (8) Erlenmeyer to collect sample; (9) Programmable switch to control the rotate of motor; (10) Programmable switch to control the temperature of environment of system; (11) pressure gauge; (12) temperature indicator; (13) safety valve; (14) pressure transducer; (15) Erlenmeyer; (16) magnetic stirrer; (17) inversed burette filled with water.