

Experimental study on gas hydrate formation from natural gas mixture



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ARTICLE INFO

Article history:

Received 18 July 2013

Received in revised form

2 January 2014

Accepted 28 January 2014

Available online 21 February 2014

Keywords:

Gas hydrate

Natural gas

Kinetics

Stirred reactor tank

ABSTRACT

In this work, gas consumption by clathrate hydrate from mixture of natural gas at different pressures and temperatures (275.15–287.25 K and 1.1–5.4 MPa) are reported. The experiments were conducted in a stirred-reactor tank in isothermal and isochoric conditions. The amount of consumed gas by the hydrate phase was determined considering the pressure reduction during the experiments. Results show the rate of gas consumption is exponentially related to the over-pressurizing of the system.

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1. Introduction

Gas hydrates are ice-like compounds, which may form when water and light gases such as methane and ethane are present together at low temperature and relatively high pressures (Skovborg and Rasmussen, 1993). Although hydrate formation has some negative connotations in the petroleum and gas processing industry, but it has the potential for many applications. Carbon dioxide capture and sequestration, gas storage, air-conditioning systems, water desalination and treatment technology, concentration of dilute aqueous solutions, and separation of different gases from flue gas streams are some applications of this phenomena (Eslamimanesh et al., 2012; Chatti et al., 2005; Makogon, 2010).

There has been major progress in thermodynamic modeling of gas hydrate since 1934 (Hammerschmidt, 1934) but the most challenging and questions about hydrate concerns how hydrates form, dissociate, and inhibit with time – kinetics (Sloan and Koh, 2008). The strong influence of heat and mass transfer on the hydrate formation makes the hydrate kinetics to be difficult to predict.

Several studies on the hydrate formation from single and two components can be found in the literature (Vysniauskas and Bishnoi, 1983, 1985; Englezos et al., 1987a,b; Clarke and Bishnoi, 2001; Bergeron and Servio, 2008, 2009; Verrett and Servio, 2012) but there is few study about multi-component mixture (Mork,

2002). In this work, we used a typical mixture of natural-gas (methane, ethane, propane and iso-butane) that are guest molecules of gas hydrates. Several experiments were conducted at different temperatures and pressures in a stirred tank reactor at constant volume to determine the rate of gas consumption. We proposed a relation between the rate of hydrate formation and over-pressurizing. Results show that gas consumption by the hydrate phase is exponentially proportional to over-pressurizing (super-saturation) of the mixture.

2. Experimental section

2.1. Materials

Table 1 reports the material purities and suppliers. Highly purified water was prepared from Ramin Power Plant (Ahwaz).

2.2. Experimental apparatus

The detailed of the apparatus is shown in Fig. 1. The unit consists of a visual double-wall stirred cell made of SS316. A 4 cm coated magnetic bar is located in the cell and is driven by an external magnetic stirrer (Labinco L-71). The stirrer was calibrated using Smart Sensor Digital Tachometer (AR926). The heat is removed from the cell by a bath circulator (Lauda R8A) that provides cooling media in the jacket of the cell. The cell is well isolated from the ambient with two insulation layers.

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Table 1
Purities and suppliers of materials.

Material	Supplier	Purity
Methane/C ₁	Persian Gas Cooperation	0.9999
Ethane/C ₂	Persian Gas Cooperation	0.9999
Propane/C ₃	Persian Gas Cooperation	0.9995
iso-Butane/iC ₄	Persian Gas Cooperation	0.9995
Deionized water	Ramin Power Plant	—

In order to perform accurate temperature measurements, two 100 Ω platinum resistance thermometer (PT-100) indicate the temperature of two levels of the cell. These PT-100s were calibrated against standard resistance. The resulting uncertainty is ± 0.1 K. The cell pressure is displayed by a Sensys pressure (0–10 MPa). The pressure measurement uncertainty is estimated to be with ± 5 kPa. All pressure gauges and the cell pressure transducer are carefully calibrated with dead weight pressure balance (DH Budenberg 580 Series).

A 50 mL (50×10^{-6} m³) SUPRA syringe is provided to introduce water to the cell (± 0.5 mL). The syringe capacity was tested by Sartorius BA110S balance. To maintain vacuum conditions before any experiment, a JB Platinum vacuum pump was employed.

During experiments, it was found that at stirring rates lower than the 300 round per minute (rpm), hydrate phase forms a layer on the gas–liquid interface. At this rate, the magnetic bar is unable to maintain sufficient mixing, and a hydrate layer is formed on the top of the liquid. In addition, for speeds upper than 450 rpm, the surface becomes rippling, and considerable bubbles are observed. Consequently, all experiments were conducted at 350 rpm to ensure satisfactory mixing in addition to prevent from rippling of the surface and bubbling in the aqueous phase. The stirrer was calibrated using Smart Sensor Digital Tachometer (AR926).

The analytical work was carried out using a gas chromatograph (Younglin Model YL6100) equipped with a micro thermal conductivity detector (μ TCD - VICI), connected to a data-acquisition system (AUTOCHRO DATA MODULE). Two series capillary columns, HP-PLOT/Q and HP-PLOT/U (Agilent Technologies), were used to detect the composition of gas phase. The calibration was performed before by the chemical laboratory of National Iranian South Oil Company.

2.3. Experimental method

All experiments were conducted at constant aqueous and gas phase volume (isochoric conditions). 90 mL of purified water was

injected into the cell before every experiment (V_W). Prior to any experiment, the reactor cell was vacuumed two times to strip the aqueous phase from any dissolved gas. The cell is then pressurized with the gas mixture below hydrate formation pressure, and cooled to the desired temperature. As the preferred temperature is achieved, the cell pressure is raised again to the experiment pressure (P_{EXP}). The stirrer is started at a very low speed (less than 50 rpm) just to maintain uniform conditions. Once thermal equilibrium has been achieved, a sample of gas was sent to the gas chromatograph (GC). Then, the stirrer speed was set to 350 rpm and the data-acquisition was started. The data-acquisition system records all data every 14 s. In some cases (especially, high over-pressurizing conditions), the cell pressure was reduced considerably fast. The required time to monitor this reduction was about half of minute. Consequently, one-quarter of minute (about 14 s) was chosen as an appropriate sample time. Because the cell is visualized, the hydrate formation point is distinguishable. The point can be also detected as the pressure started to fall.

It was observed that the pressure reduction is considerable at the beginning of each test but as the process continues (depends on the degrees of over-pressurizing) the pressure reduction rate was decreased. This fact is the consequence of two phenomena. The first is that hydrate film above the mixture prevents from freely diffusion of gas molecules to the aqueous phase. The second is that hydrate particle numbers, and their total areas are such that they occupy a considerable amount of the gas–liquid interface. To avoid this problem, all experiments are left to continue until about 100 kPa pressure reduction. At the end of the experiment, the stirrer turned off and a sample gas was quickly sent to be analyzed by the GC.

3. Modeling

3.1. Rate of gas consumption

The experimental study is based on the determination of the amount of gas phase with time. Thus, any change in the moles of the gas phase is considered as the consumption by the hydrate phase. The cell temperature is kept constant and the pressure is recording. It is assumed that the gas phase volume has no change during each run. Therefore, the total moles of the gas phase can be calculated if the composition of vapor is available. SRK EOS as an appropriate equation of state was used to determine the compressibility factor and consequently, moles of the gas phase (Soave, 1972; Danesh, 2003). The binary interaction parameters are reported in Table 2.

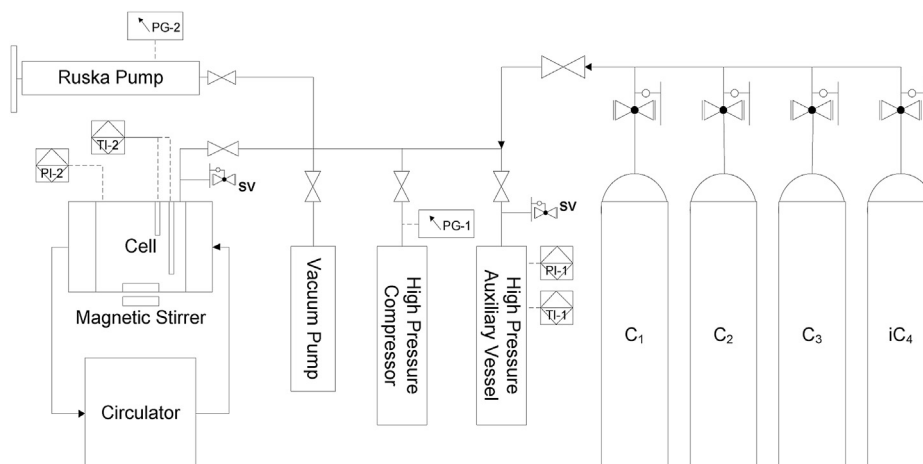


Fig. 1. Schematic Diagram of the Apparatus, PG: Pressure gauge, SV: Sample Valve, TI and PI: Temperature and pressure indicators.

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