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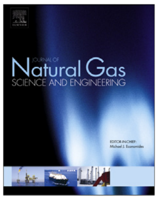

Formation kinetics & phase stability of double hydrates of C_4H_8O and CO_2/CH_4: A comparison with pure systems

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Gas hydrate based technology plays a key role in capturing carbon dioxide (CO_2) or methane (CH_4) gas molecules from its source locations. The parameters like hydrate phase stability, formation kinetics and gas uptake capacity (hydrate yield) are measured for carbon dioxide (CO_2) and methane (CH_4) at different initial gas pressures. The behaviour is also compared with double hydrates, prepared using 6 mol% of tetrahydrofuran (C_4H_8O -THF) aqueous solution. Measured thermodynamic phase boundary points for the hydrates with single guest molecules (CO_2 or CH_4) concur with the literature data. However, the phase stability of double hydrates with THF + CO_2/CH_4 appeared to be controlled by the stability of THF hydrates. Hydrate formation kinetics is faster in double hydrates than corresponding pure hydrates. Further, the yields in double hydrates with CH_4 guest molecule show increasing trends with the gas pressure, whereas, it remains unchanged in double hydrates with CO_2 guest molecule beyond some gas pressure. This is attributed to the occupancy of vacant cages by the gas molecules.

1. Introduction

Global energy needs and climate changes induced due to increased greenhouse gas emissions demand exploration for newer energy sources and also meticulous planning on the CO_2 emissions. Naturally occurring gas hydrates (clathrate compounds) offer a dependable solution in partially fulfilling increasing fuel gas demand. Gas hydrates are non-stiochiometric inclusion compounds, belonging to a group of solids known as clathrates, comprising of a host network, made up of hydrogen-bonded water molecules consisting of vacant cavities, occupied by guest gas molecules of suitable size (Sloan and Koh, 2008). These are normally formed at high pressure and low temperature conditions in the vicinity of freezing point of water. Three common structures, structure I (sI), structure II (sII), and structure H (sH) are known to form as a function of size and shape of the guest molecules (Sloan, 2003). The size of the guest molecules ranging from 3.91Å to 5.79 Å and methane is the most predominant constituent in natural gas hydrates. Conservative estimates reveal that the fuel gas entrapped in this form can cater for the global energy requirements at least for the next 200 years, even with the extraction of 10% fuel gas from the available resources (Makogon et al., 2007). However, the gas extraction from gas hydrate deposits poses many technological challenges because their existence in difficult geological terrain. In principle, the gas hydrate phase can be destabilized by decreasing the pressure (depressurization) or increasing the local temperature (thermal stimulation). Another method is the molecular substitution, wherein the CH_4 molecules from the clathrate cages are replaced by the CO_2 molecules. For all such applications it is important to assess the hydrate formation ability and its structural stability at different pressures (Ohgaki et al., 1996). The scope of this work deals with probing the formation kinetic of pure hydrates with CO_2 and CH_4; and corresponding double hydrates with tetrahydrofuran (THF). It is known that hydrate forming additives, such as THF or amines, are thermodynamic promoters for CH_4/CO_2 hydrates, even though a structural change is impending in double hydrates (Chari et al., 2012). A clathrate hydrate with CO_2 as guest is also a favourable means to store greenhouse gas (CO_2) for long period times at some favourable location on ocean floor (Caldetra and Wickett, 2005; Lee et al., 2002). Even though, gas hydrates with CH_4 or CO_2 crystallize into sI and because of molecular size constraints the smaller cages in CO_2 hydrates remain vacant, while

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the large cages are predominately occupied by CO_2 molecules. On the other hand, in methane hydrates both cages are occupied by CH_4 molecules (Kim et al., 2006).

Hydrate based technology has been adopted in greenhouse gas separation, storage and transportation applications. Normally CO_2 and CH_4 hydrates are stable under high pressure and low temperature conditions, which significantly defer from the ambient conditions. Usually hydrate formation with lesser deviations from the ambient pressure, temperatures are often preferred for such applications. Therefore, some additional organic compounds like tetrahydrofuran (THF), 1, 4-dioxane (DXN), and acetone etc., are used in hydrate formations. They act as hydrate promoters to lower the hydrate equilibrium pressure (at a given temperature) and/or to increase the hydrate equilibrium temperature at a given pressure (Pahlavanzadeh et al., 2012; Mohammadi et al., 2010). Usage of such thermodynamic promoters are recently been tested at laboratory in developing CH_4 separation/extraction process from coal mine methane (Zhang and Wu, 2010; Lim et al., 2013; Giavarini et al., 2008). Among all such thermodynamic promoters, double hydrates with THF have shown higher thermodynamic stability of hydrate phase and thus are favourite system in separation/storage applications.

Chun and Lee (1996) reported on the hydrate formation kinetics in CH_4/CO_2 and water system in a semi-batch stirred reactor. They observed that the formation kinetics in CO_2 hydrates is faster than corresponding methane hydrates (2–3.5 MPa); and their results are consistent with the model developed by Englezos et al. (1987). Adisasmito et al. (1991) measured the phase equilibrium data of the CO_2/CH_4 hydrates. Lee et al. (2002) studied the hydrate phase behaviour and the formation kinetics of CO_2+H_2O system with NaCl or clay. They conclude that hydrate equilibrium line shifted to inhibition side and the formation kinetics is slower in the presence of NaCl or clay compare to pure CO_2 hydrate system. Susilo et al. (2008) carried out simulations on CH_4+H_2O hydrate system with various concentrations of THF/propane in double hydrates to measure the methane gas content and phase stability conditions. The phase stability and formation kinetics in such hydrates are significantly altered to higher temperatures and lower pressure conditions when co-guests such as THF or propane are also present in hydrate forming system (Susilo et al., 2008; Kumar et al., 2008). Seo et al. (2008) measured the hydrate phase equilibrium for CO_2 and H_2O system, in the presence of thermodynamic promoters like THF, Propylene oxide and DXN. They found that a shift in the hydrate equilibrium conditions to higher temperature and lower pressure compared to the pure CO_2 hydrates; and among these promoters THF exhibits a larger shift in the phase stability point. Similar observations are reported by Chari et al. (2012) on the double hydrates involving methane molecules. They observed that mixed hydrates formed with methane and THF/t-$BuNH_2$ in sII stoichiometry dissociates at much higher temperatures (THF − 18 °C and t-BuNH2 − 12 °C) compared to pure methane hydrate. Sabil et al. (2010a, b) conducted experiments to measure the phase equilibrium data for pure (CO_2+H_2O) and double hydrate systems (CO_2+THF + H_2O), at different CO_2 pressures range 1–7.5 MPa. Their measurements also reported significant shift in the phase stability points for double hydrates with THF + CO_2. Further, they carried out experiments on kinetics of formation and amount of CO_2 consumption in pure and double hydrates Sabil et al. (2010a). They reported significant reduction in CO_2 uptake in double hydrates. Recently Lee et al. (2012) also investigated the hydrate phase equilibrium behaviours of THF + CH_4, THF + CO_2, CH_4+CO_2, and THF + CO_2+CH_4 over wide ranges of temperature, pressure, and concentrations. They reported that dissociation conditions of THF + CH_4 and THF + CO_2 hydrates are shifted to lower pressures and higher temperatures from the dissociation boundaries of pure CH_4 and pure CO_2 hydrates. From their Raman spectroscopic measurements concluded that CO_2 molecules preferentially occupy large cages of sI hydrate forming system; while it could be encaged in small cages as well in sII hydrate forming systems. This interpretation is consistent with the earlier report (Shin et al., 2009). They also conclude that CO_2 molecules occupy large $5^{12}6^2$ cages of sI in pure hydrate system, while they occupy the small 5^{12} cages of the sII in CO_2-THF and CO_2-DXN hydrate system.

In the present work we have compared the formation kinetics of CO_2 and CH_4 pure systems with THF-CO_2 and THF-CH_4 hydrates and probed the influence of THF on the formation kinetics, yield and stability conditions for 6 mol% of THF concentration. Additionally, we have confirmed the presence of CO_2 molecules in pure and double hydrate system by using Raman spectroscopy.

2. Experimental method

2.1. Materials

High purity (99.95%) gases (CO_2 and CH_4) and tetrahydrofuran (98%) supplied by Qualigens fine chemicals, India were used in this study. Dissolved gases from ultrapure water were removed by continuous evacuation. The required amount of pure water was measured by using Metler Toledo (AB104-S) accurate analytical balance. The THF concentration in aqueous solution was kept around 6 mol%, about 10% higher than ideal stoichiometric composition of sII THF hydrates, because of its volatile nature.

2.2. Experimental apparatus

Detailed description of experimental layout and procedure has been described in previous report by Chari et al. (2012). Briefly, the main part of the apparatus is an SS-316 cylindrical vessel, which can withstand pressures up to 10 MPa. The volume of vessel is 100 ml. A stirrer with variable speed was installed in the vessel to agitate the fluids and hydrate crystals inside it. All the experiments were conducted with continuous stirring at 400–500 rpm. Cold fluid (water + glycol mixture) was circulated around the vessel with the help of Lab Companion (RW-0525G) circulator, to maintain the temperature inside it at a desired level. A platinum resistance thermometer (Pt100) inserted into the vessel was used to measure temperatures and check for equality of temperatures within temperature measurement uncertainties, which is estimated to be less than 0.2 K. The pressure in the vessel was measured with a WIKA pressure transducer (WIKA, type A-10 for pressure range 0–16 MPa).

The vessel containing aqueous solution (~30 ml pure water/aqueous solution) was immersed into the temperature controlled bath and the gas was supplied from a cylinder to desired level using Teledyne ISCO Syringe pump (Model 100DX). Note that the vessel was evacuated before introducing any aqueous solution and gas. After obtaining temperature and pressure stability (far above from the hydrate formation region), the valve inline connecting the vessel and the ISCO pump/cylinder was closed. Subsequently, temperature was slowly decreased to form the hydrate and hydrate formation in the vessel was detected by pressure drop. The temperature was then increased in steps of 1.0 K. At each step, temperature was kept constant for longer time to achieve equilibrium state. In this way, a pressure temperature diagram was obtained for each experimental run, from which we determined the hydrate formation and dissociation pattern. If temperature is increased in the hydrate-forming region, hydrate crystals partially dissociate, thereby substantially increasing the pressure. If the temperature is increased outside the hydrate region, only a smaller increase in the pressure is observed as a result of the change in phase equilibria of