



Thermodynamic promotion of carbon dioxide–clathrate hydrate formation by tetrahydrofuran, cyclopentane and their mixtures



Peter Jørgensen Herslund^a, Kaj Thomsen^a, Jens Abildskov^b, Nicolas von Solms^{a,*}, Aurélie Galfré^c, Pedro Brântuas^c, Matthias Kwaterski^c, Jean-Michel Herri^c

^a Department of Chemical and Biochemical Engineering, Center for Energy Resources Engineering (CERE), Technical University of Denmark, Kgs. Lyngby DK2800, Denmark

^b Department of Chemical and Biochemical Engineering, Computer Aided Process Engineering Center (CAPEC), Technical University of Denmark, Kgs. Lyngby DK2800, Denmark

^c Ecole Nationale Supérieure des Mines de St-Etienne, 158 Cours Fauriel, 42023 St-Etienne, France

ARTICLE INFO

Article history:

Received 10 December 2012

Received in revised form 21 May 2013

Accepted 24 May 2013

Keywords:

Gas hydrates

Carbon dioxide capture

Tetrahydrofuran

Cyclopentane

Thermodynamic promoter

ABSTRACT

Gas clathrate hydrate dissociation pressures are reported for mixtures of carbon dioxide, water and thermodynamic promoters forming structure II hydrates.

Hydrate (H)–aqueous liquid (L_w)–vapour (V) equilibrium pressures for the ternary system composed of water, tetrahydrofuran (THF), and carbon dioxide (CO_2), with 5.0 mole percent THF in the initial aqueous phase, are presented in the temperature range from 283.3 K to 285.2 K. At 283.3 K, the three-phase equilibrium pressure is determined to be 0.61 MPa (absolute pressure).

Four-phase hydrate (H)–aqueous liquid (L_w)–organic liquid (L_a)–vapour (V) equilibrium data are presented for the ternary system of water–cyclopentane–carbon dioxide at temperatures ranging from 285.2 K down to 275.5 K.

New four-phase H– L_w – L_a –V equilibrium data for the quaternary system water–THF–cyclopentane–carbon dioxide are presented in the temperature range from 275.1 K to 286.6 K. It is shown that upon adding THF to the pure aqueous phase to form a 4 mass percent solution, the equilibrium pressure of the formed hydrates may be lowered compared to the ternary system of water, cyclopentane and carbon dioxide.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Gas clathrate hydrates, more commonly known as gas hydrates, are solid solutions of small guest molecules physically adsorbed into cavities formed by hydrogen bonded water clusters. These solid compounds form when the constituents come into contact at conditions of low temperature and/or high pressure (Sloan, 2003). Temperature and pressure conditions, at which the hydrates form, depend on the physical and chemical properties of the guest molecule, assuming that the water phase is pure. Impurities or additives dissolved in the aqueous phase may also affect the gas hydrate equilibrium conditions as well as the formation kinetics.

Gas hydrates are often referred to as non-stoichiometric solid inclusion bodies, where water (host) forms a lattice by hydrogen bonding (Koh et al., 2009; Sloan, 2003; Sum et al., 2009). The lattice formation generates a number of empty cavities, in which small molecules (guests) may be encapsulated. Several structures are

known, the most common being structures sI, sII and sH. The pure, empty hydrate water lattice itself is a thermodynamically unstable structure, and it is the interactions between water and guest molecules stabilise the lattice structure (Sum et al., 2009).

1.1. Gas hydrate formation with thermodynamic promotion

When the occurrence of gas hydrates in the petroleum industry was discovered, an increased effort was made to map their structures and to find ways of avoiding their formation in oil and gas pipelines.

Recently, gas hydrates have received new interest due to their relatively high gas/energy density. Whereas most previous efforts were directed towards looking for ways to avoid hydrate formation (hydrate inhibition), the focus is now also on finding ways to promote their formation at moderate temperatures and pressures (hydrate promotion). Sun et al. (2011) and Eslamimanesh et al. (2012) have reviewed recent advances in gas hydrate research including applications of promoted gas hydrate formation in processes for methane/natural gas storage, fuel gas (hydrogen) storage and gas separation (e.g. carbon dioxide capture).

* Corresponding author. Tel.: +45 4525 2867; fax: +45 4588 2258.
E-mail address: nvs@kt.dtu.dk (N. von Solms).

1.2. Thermodynamic gas hydrate promoters

A thermodynamic promoter is here defined as a component that participates actively in the hydrate formation process and readily enters the hydrate structure at higher temperature and lower pressure than in the unpromoted hydrate.

Whereas the mechanism for thermodynamic inhibition of hydrate formation is a consequence of a change in water activity due to hydrogen bonding between hydrate inhibitors (mainly methanol, monoethylene glycol or diethylene glycol) and water, thermodynamic promotion of gas hydrates is a consequence of the active formation of mixed promoter/gas hydrates under moderate conditions of temperature and pressure. The hydrates formed in that way then serve as a storage medium for gas-like components but may also contain significant amounts of the added promoter.

In this work, only hydrate promoters forming classical hydrate structures (mainly sII and sH, where the promoter molecules partly enter the appropriately sized cavities), have been considered. Hydrate promoters such as the tetra-*n*-butyl ammonium halides (TBAB, TBACl, TBAF etc.) which form semi-clathrates, where the promoter actively takes part in the formation of the lattice structure of water molecules, have not been considered.

Over the years many heavy hydrocarbon compounds have been investigated for their ability to form gas hydrates in the presence of small gas molecules. A summary including hydrate dissociation pressure data for most of the binary methane-/heavy hydrocarbon-based hydrate systems (mainly sH forming systems) investigated was presented by Sloan and Koh (2008). Most of these heavy hydrocarbons are – due to their hydrophobic characteristics – only partially miscible with water, giving rise to liquid–liquid phase separation. Hence, the experimental data represent hydrate (H)–aqueous liquid (L_w)–organic liquid (L_a)–vapour (V) four-phase equilibria.

Several hydrophilic, organic compounds are also known for forming hydrates at moderate temperatures and pressures. Saito et al. (1996) investigated the possibility of storing natural gas in the form of hydrates by using either tetrahydrofuran (THF) or acetone to lower the equilibrium pressure of the mixed hydrates. They showed how the three-phase H– L_w –V equilibrium pressure depends on the promoter concentration in the liquid phase co-existing with the hydrate phase. A minimum in the observed hydrate dissociation pressures was detected at a promoter concentration in the aqueous liquid phase of approximately 5 mole percent, close to the stoichiometric concentration of the sII hydrate structure with complete occupation of the large cavity by the promoter molecules.

De Deugd et al. (2001) compared the promoting effect of three water-soluble hydrate formers constituting mixed hydrates with methane. The three hydrate formers were THF, 1,3-dioxolane and tetrahydropyran. From their results, De Deugd et al. concluded that five sided cyclo-ether structures (THF) are more efficient sII hydrate stabilisers than six sided cyclo-ether structures (tetrahydropyran). Furthermore, they inferred from their data that one oxygen atom in the five sided ring structure (THF) stabilises the sII hydrate better than five sided ring structures with two oxygen atoms (1,3-dioxolane). De Deugd et al. explained these findings by the differences in physical size and polarity of the three compounds and suggested cyclopentane as a possible promoter for the formation of sII hydrate. Tohidi et al. (1997) had already shown this by measuring the promoting effect on the dissociation pressures of methane or nitrogen hydrates by adding cyclopentane to binary systems of water and gas.

Ohmura et al. (2005) measured hydrate dissociation pressures for two methyl-substituted cyclic ethers (2-methyltetrahydrofuran and 3-methyltetrahydropyran) with methane. These ethers were soluble in water to some extent, but not fully miscible with water,

like THF. Even though these methyl-substituted cyclic ethers were more interesting promoters for hydrate-based gas storage applications from an environmental impact point of view, they were unfortunately less efficient hydrate promoters in comparison with their non-substituted counterparts.

Tsuji et al. (2004) showed the importance of water solubility in order to obtain high formation rates of hydrates. They measured formation rates of mixed promoter/methane hydrates by spraying an aqueous phase into a methane gas phase at constant pressure. It was concluded that the gas uptake into the sH hydrate phase was promoter dependent but they also found that, in their process configuration, the largest gas uptakes were generally obtained in systems with high promoter concentrations in the aqueous phase.

In this work the specific case of capturing carbon dioxide (CO_2) using thermodynamically promoted gas hydrate formation is investigated. The two hydrate promoters, cyclopentane and THF were chosen for the study. They differ in their fluid phase behaviour in aqueous systems, but have similar properties in the hydrate phase. THF appears to be the most efficient of the known water-soluble sII hydrate promoters and cyclopentane appears to be the most efficient of all known sII hydrate promoters. Hence, THF and cyclopentane are the hydrate promoters selected in this work.

1.2.1. Tetrahydrofuran—A hydrophilic hydrate promoter

Tetrahydrofuran is a five-sided cyclic ether structure that has received much attention in the literature not only due to its properties as an organic solvent, but also due to the fact that it forms structure II hydrates with water. At ambient conditions, THF and water are completely miscible in the liquid state, i.e., upon mixing THF and water, homogeneous liquid mixtures are formed over the whole composition range. However, closed loop miscibility gaps (liquid–liquid phase splits) have been observed at temperatures above 345 K and slightly elevated pressures (Riesco and Trusler, 2005).

Several publications are available in the literature, presenting THF as a possible promoter in pre- (Lee et al., 2010; Linga et al., 2007a, 2007b; Zhang et al., 2009) or post combustion (Giavarini et al., 2010; Kang and Lee, 2000; Kang et al., 2001; Linga et al., 2007b, 2008, 2010) hydrate-based CO_2 capture processes. However, only a few publications provide detailed phase equilibrium data for the ternary system of water, THF, and CO_2 , especially at low temperatures and THF concentrations of approximately 17.4 mass percent (5 mole percent) in the aqueous phase (Delahaye et al., 2006; Sabil et al., 2010; Seo et al., 2008). Such data can provide information on the true ability of THF promoted sII hydrates to incorporate sufficient amounts of CO_2 in order to establish a feasible capture process operating at temperatures close to the freezing point of water.

In separation attempts applied to gas mixtures containing CO_2 and nitrogen, one of the main conclusions was that the selectivity of CO_2 over N_2 in the hydrate phase is lowered by the presence of THF compared to the non-promoted systems (Kang and Lee, 2000). The highest CO_2 selectivities were obtained when operating at low temperatures. Hence it is of interest to investigate how binary hydrate systems of THF and CO_2 behave in the low temperature region, not only with respect to the inclusion of CO_2 in the solid phase but also with respect to the pressure requirements needed to form mixed hydrates at these conditions.

Delahaye et al. (2006) measured hydrate dissociation P – T conditions as well as heats of dissociation for the ternary system of water, THF and CO_2 . In addition, the T – x diagram for the binary sub-system of water and THF was experimentally determined at atmospheric pressure for reference and for modelling purposes. In the binary system {water + THF}, the melting point (dissociation temperature) of the THF sII hydrate formed from a 19.17 mass percent (approximately 5.9 mole percent) THF aqueous solution was determined to be 277.9 K.

Download English Version:

<https://daneshyari.com/en/article/8092084>

Download Persian Version:

<https://daneshyari.com/article/8092084>

[Daneshyari.com](https://daneshyari.com)