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Semi-clathrate hydrate phase equilibrium measurements for the CO_2+H_2/CH_4+tetra-n-butylammonium bromide aqueous solution system

Amir H. Mohammadi [a,b,*], Ali Eslamimanesh [c,1], Dominique Richon [b,d]

[a] MINES ParisTech, CEP/TEP - Centre Énergétique et Procédés, 35 Rue Saint Honoré, 77305 Fontainebleau, France
[b] Thermodynamics Research Unit, School of Chemical Engineering, University of KwaZulu-Natal, Howard College Campus, King George V Avenue, Durban 4041, South Africa
[c] MINES ParisTech, CEP/TEP—Centre Énergétique et Procédés, 35 Rue Saint Honoré, 77305 Fontainebleau, France
[d] Department of Biotechnology and Chemical Technology, School of Science and Technology, Aalto University, Aalto, Finland

HIGHLIGHTS

- Phase equilibria of semi-clathrate hydrates of mixtures of gases were measured.
- The data are for the CO_2+H_2/CH_4+water/TBAB aqueous solution systems.
- The isochoric pressure search method was pursued for performing the measurements.
- The hydrate promotion effects of TBAB are discussed.

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ABSTRACT

In this communication, clathrate/semi-clathrate hydrate dissociation conditions for the systems containing mixtures of CO_2 (0.1481/0.3952/0.7501 mol fraction)+H_2 (0.8519/0.6048/0.2499 mol fraction) in the presence of water or 0.05 and 0.30 mass fractions tetra-n-butylammonium bromide (TBAB) aqueous solutions and CO_2 (0.4029 mol fraction)+CH_4 (0.5971 mol fraction) in the presence of water, 0.05 and 0.3 mass fractions TBAB have been measured and are reported. An apparatus comprising a high pressure equilibrium cell as the main part has been employed for the measurements following the isochoric pressure-search method. The range of conditions for the measurements are 275.5–292.8 K up to 15.91 MPa. Significant decrease in operating pressure of gas hydrate formation for separation of CO_2 from the corresponding gas mixtures is observed due to the promotion effects of TBAB.

1. Introduction

Clathrate (gas) hydrates are inclusion compounds composed of H_2O and guest species (Sloan and Koh, 2008). They are normally stabilized by the guest molecules (can be either gas or particular liquids under room conditions) enclathrated in the hydrogen-bonded water cages (Sloan and Koh, 2008). At relatively high pressures and low temperatures, water molecules form various crystalline structures generally depending on the size and shape of the guest molecule(s) (Sloan and Koh, 2008; Eslamimanesh et al., 2011a,b). Structures I (*s*I), II (*s*II), and H (*s*H) are known to form as three common structures of clathrate hydrates.

Despite the obstructions of gas hydrate formation in petroleum industry, positive applications of these compounds e.g. in carbon dioxide (CO_2) capture and sequestration, gas storage, air-conditioning systems in the form of hydrate slurry, water desalination technology, concentration of dilute aqueous solutions, oil and gas separation, separation of different gases, ionic liquids recovery etc. (Belandria et al., 2011a; Khokhar et al., 1998; Shimada et al., 2005; Aladko et al., 2003; Ogoshi and Takao, 2004; Dabrowski et al., 2009; Englezos and Lee, 2005; Englezos, 1993; Eslamimanesh et al., 2012; Mohammadi et al., 2012) have been also proposed especially since the past decade.

Significant amounts of carbon dioxide, as a major contributor to the overall greenhouse effects, are currently emitted to the atmosphere due to combustion of fossil fuels such as coal, oil, and

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[*] Corresponding author at: MINES ParisTech, CEP/TEP - Centre Énergétique et Procédés, 35 Rue Saint Honoré, 77305 Fontainebleau, France.
E-mail address: a.h.m@irgcp.fr (A.H. Mohammadi).
[1] Current address: Department of Chemical & Biomolecular Engineering, Clarkson University, Potsdam, NY 13699-5705, USA.

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natural gas (Eslamimanesh et al., 2012; Mohammadi et al., 2011, 2012; Miller and Smythe, 1970; Bacher, 2002; Hall et al., 2003; International Panel on Climate Control (IPCC), 2005; Gough et al., 2002; Yang et al., 2008). Global warming, catastrophic environmental effects including drastic climate change and so forth are among the most significant consequences of greenhouse effects. Therefore, separation of carbon dioxide from gas streams is of particular interest for the industry in the environmental scope.

Some industrial gas streams may have considerable amounts of hydrogen (H_2). For instance, the integrated coal gasification cycle (ICGC) may produce gas flows containing mixtures of CO_2 and H_2 after converting the gas, generated in the gasifier or the streams produced in steam reforming processes (Li et al., 2010; Belandria et al., 2011a; Descamps et al., 2005). Therefore, industrially feasible processes are required to design for separation of these two species from the aforementioned mixtures as well.

On the other hand, methane is the major component of natural gas and natural gas reserves in the form of hydrates in the earth, as well as emissions in the form of cold bed methane (CBM) discharging from coal seams (Eslamimanesh et al., 2012). Consequently, separation of methane from emitted industrial gases has attracted significant attention in the last few decades (Eslamimanesh et al., 2012).

General (or commercial) methods, proposed in open literature to separate carbon dioxide from gas streams, mainly include alkanolamine, particularly MEA (methyl ethyl amine), absorption, PSA (pressure swing absorption) process, cryogenic operations, membrane separation, oxy-combustion process and so forth (Seo and Kang, 2010). However, relatively high energy consumption or probability of corrosions in the processes facilities may be the potential drawbacks of such processes (Seo and Kang, 2010). Consequently, searching for less energy-intensive, environmental-friendly, and more economic separation processes are undergone by various research groups world-wide.

Hydrate crystallization (formation) method has recently attracted much attention to separate carbon dioxide from gas streams (Eslamimanesh et al., 2011a, 2011b, 2012; Belandria et al., 2011a, 2011b, 2011c; Shimada et al., 2005; Mohammadi et al., 2011, 2012; Li et al., 2010; Descamps et al., 2005; Seo and Kang, 2010; Peng and Zhuang, 2011; Feron and Hendricks, 2005; Kang and Lee, 2000; Linga et al., 2007; Papadimitriou et al., 2011; Sabil et al., 2010a, 2010b, 2010c; Mooijer-Van Den Heuvel et al., 2001; Strobel et al., 2006, 2009a, 2009b; Sugahara et al., 2005, 2009; Sun et al., 2010; Wu et al., 2010; Zhang and Wu, 2010; Lu et al., 2009; Zhang et al., 2006, 2008; Zhang et al., 2009; Shimada et al., 2003; Fukushima et al., 1999; Shin et al., 2009; Paricaud, 2011; Acosta et al., 2011; Separation of CO_2; by Hydrate Absorption (SECOHYA) Project, 2007–2011; Kumar et al., 2009; Kim and Lee, 2005; Hashimoto et al., 2006; Zhang et al., 2009; Lee et al., 2010). The affinity of various hydrate formers to be trapped in the water hydrogen-bonded cages are different. Therefore, due to the difference in the tendency of CO_2 and other gases to be captured in the hydrate cages, when clathrate/semi-clathrate hydrate crystals are formed from a corresponding mixture, the hydrate phase can be enriched in CO_2 while the concentration of other gases can be increased in the gas phase. For instance, due to extremely difference in hydrate formation (dissociation) pressure of CO_2 with that of H_2 at the same temperature conditions, CO_2 has more general tendency to be trapped in the water hydrogen-bonded cages leaving, as a consequence, a CO_2-lean gas phase. The hydrate phase can be later dissociated by depressurization and/or heating resulting the recovery of CO_2 (Eslamimanesh et al., 2012; Mohammadi et al., 2011, 2012; Belandria et al., 2011a).

However, the required pressure for the gas hydrate formation is relatively high and may result in excess costs for the industry (Eslamimanesh et al., 2012; Mohammadi et al., 2012). Gas hydrate promoters are normally added to such processes to reduce the required hydrate formation pressure or increase the formation temperature along with possible modification of hydrate cages selectivity for enclathration of the gas molecules of interest (Eslamimanesh et al., 2011a, 2012; Mohammadi et al., 2011). Chemical additives such as tetrahydrofuran (THF), cyclopentane, acetone, etc. (Mohammadi et al., 2012; Papadimitriou et al., 2011; Sabil et al., 2010a, 2010b, 2010c; Mooijer-Van Den Heuvel et al., 2001; Strobel et al., 2006, 2009a, 2009b; Sugahara et al., 2009; Sun et al., 2010; Wu et al., 2010; Zhang and Wu, 2010; Lu et al., 2009; Zhang et al., 2009; Zhao et al., 2008; Zhang et al., 2006) may be used as hydrate promoters without taking part in the structures of the water cavities. On the other hand, tetra-n-butylammonium salts like tetra-n-butylammonium bromide (TBAB) may significantly reduce the required hydrate formation pressure by taking part in the structure of hydrogen-bonded networks of water to form particular structures called "semi-clathrate hydrates" (Eslamimanesh et al., 2012; Mohammadi et al., 2012; Shimada et al., 2003; Fukushima et al., 1999; Shin et al., 2009; Paricaud, 2011; Acosta et al., 2011). These promoters, which are normally environmental friendly, have been demonstrated to have more gas storage capacity than the organic hydrate promoters such as THF (Eslamimanesh et al., 2012). Another element to consider is that they are generally less volatile than promoters like THF and may prevent non-negligible amounts of vaporization loss of hydrate promoters during separation processes (Eslamimanesh et al., 2012; Mohammadi et al., 2012).

In order to design separation processes using clathrate/semi-clathrate hydrate crystallization, reliable phase equilibrium data are required. Tables 1 and 2 provide summaries of almost all experimental studies on hydrates for mixtures of CO_2+H_2 or CH_4 in the presence of TBAB aqueous solution that are available in open literature. It seems to be obvious that it is of great attraction to generate more experimental phase equilibrium data to clarify complex phase behavior of semi-clathrates, tune the future thermodynamic models, and for the investigation of the relevant separation capabilities through application of these structures. Consequently, in this study, the clathrate/semi-clathrate hydrate dissociation conditions for the CO_2 (0.1481/0.3952/0.7501 mol fraction)$+H_2$ (0.8519/0.6048/0.2499 mol fraction) and CO_2 (0.4029 mol fraction)$+CH_4$ (0.5971 mol fraction) systems in the presence of water/different concentrations of TBAB aqueous solutions are reported.

2. Experimental section

2.1. Materials

Table 3 reports the chemicals used in the present study, along with their suppliers, and their purities/compositions. The chemicals were used without any further purification. Aqueous solutions were prepared following the gravimetric method, using an accurate analytical balance (mass uncertainty ± 0.0001 g).

2.2. Apparatus

The experimental set-up (designed and built in-house) clearly described in our previous works (Belandria et al., 2011a,b,c; Mohammadi et al., 2011, 2012; Eslamimanesh et al., 2011a) have been herein employed for the measurements. A cylindrical vessel (the main part of the apparatus) made of austenitic stainless steel, which withstands hydrogen embrittlement is used at temperatures ranging from 233 to 373 K up to 40 MPa. This apparatus was designed on the basis of the "static-analytic" technique. Its equilibrium cell has an inner volume of 201.5 ± 0.5 cm^3 and has two sapphire windows. A