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Separation of methane-ethylene via forming semi-clathrate hydrates with TBAB

Qiang Sun, Jinzhao Zhang, Yang Luo, Xuqiang Guo*, Aixian Liu

State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing, 102249, China

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ABSTRACT

The formation conditions of CH_4-C_2H_4 hydrate in water and 10 wt% tetra-n-butyl ammonium bromide (TBAB) solution were measured in this work. On this basis, the equilibrium separation of CH_4-C_2H_4 via TBAB semi-clathrate hydrate formation was conducted at constant temperature and pressure. The results show that the influence of TBAB on the formation of CH_4-C_2H_4 hydrate changes with temperature. At low temperature, TBAB forms semi-clathrate hydrate and acts as a promoter for CH_4-C_2H_4 hydrate. At high temperature, TBAB exists as a salt compound and behaves as an inhibitor for CH_4-C_2H_4 hydrate. CH_4-C_2H_4 can be efficiently separated via TBAB semi-clathrate hydrate formation under proper temperature and pressure. The results indicate that C_2H_4 can not be encased in the dodecahedral cages of TBAB hydrate. Therefore, the concentration of C_2H_4 in hydrate could be as low as 0.55 mol% and the recovery of C_2H_4 could reach 99.85% in equilibrium gas.

1. Introduction

Ethylene is an important raw material in petrochemical industry. The demand for ethylene has been growing steadily (Chen et al., 2005). Currently, the main production technology of ethylene is stream cracking of hydrocarbon feedstock such as naphtha (Ren et al., 2006). Meanwhile, refinery off-gases such as catalytic cracking gas and delayed coking gas are released with substantial ethylene and other hydrocarbon gases. Therefore, recovery of ethylene from refinery off-gases is of great economic significance. However, ethylene is difficult to separate from other gases such as methane and hydrogen with which it is normally associated (Ludwig, 1951). The concentrations of methane and hydrogen are usually more than 40 mol% (Huang et al., 2006). These contaminant gases in refinery off-gases necessitates the use of large and expensive equipment for the separation of the ethylene, like cryogenic distillation (Eldridge, 1993), liquid absorption (Sánchez et al., 2009), pressure swing adsorption (Yang et al., 2008) and membrane separation (Khan et al., 2010). Consequently, the separation of CH_4-C_2H_4 gas mixture by hydrate method (Sloan and Koh, 2008; Chen et al., 2008) was investigated in this work.

Hydrates, also called as clathrate hydrates, are a group of nonstoichiometric, ice-like crystalline compounds formed by water and guest molecules under favorable temperature and pressure (Englezos, 1997). Hydrate-based gas separation method has attracted great attention and obtained extensive research in the past decades (Happel et al., 1994; Tulk et al., 1999; Vorotyntsev et al., 2001; Kamata et al., 2005; Li et al., 2010a; Eslamimanesh et al., 2012). Furthermore, the application of hydrate thermodynamic promoter effectuates the mild condition and low energy consumption for hydrates formation and dissociation. Considerable efforts have been made to investigate the effects of thermodynamic promoters on hydrate crystallization process (Belandria et al., 2012). Hydrate thermodynamic promoters can be divided into two categories: (1) chemicals that have no effect on the structures of water such as tetrahydrofuran (THF), cyclopentane (CP) and others (Papadimitriou et al., 2011; Sabil et al., 2010a, 2010b), and (2) chemicals that change the structures of the cages in hydrates such as tetra alkyl ammonium salts (Makino et al., 2010; Shin et al., 2009; Song et al., 2009; Fan et al., 2009; Deschamps and Dalmazzone, 2009).

Tetra-n-butylammonium bromide (TBAB) is a quaternary ammonium salt that has been proposed as an environmental friendly hydrate promoter for gas separation (Shimada et al., 2003), storage (Aladko and Dyadin, 2004; Duc et al., 2007) and transport (Hashimoto et al., 2006) applications in the form of semi-clathrate hydrates. In TBAB semi-clathrate hydrates, the hydrate cage structure is broken in order to enclose the large TBA^+ cation. The anion

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* Corresponding author.
E-mail address: guoxq@cup.edu.cn (X. Guo).

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Br^- participates in the hydrogen-bonded water framework (Eslamimanesh, 2012). The X-ray analysis results of TBAB hydrate show that it has empty small dodecahedral cages (Shimada et al., 2003). Therefore, TBAB semi-clathrate hydrate can be used as molecular sieves to trap small gas molecules which fit in these dodecahedral cages, such as CH_4, CO_2, N_2, and H_2S, etc (Li et al., 2010b; Xu et al., 2013; Liu et al., 2015; Chen et al., 2015). TBAB solution with the concentration of 10 wt% is widely applied to form TBAB-gas semi-clathrate hydrate in consideration of both the thermodynamic promoting effect and gas storage capacity of hydrate. Consequently, the separation of CH_4-C_2H_4 via hydrate formation in 10 wt% TBAB solution was investigated in this work to develop an efficient approach for the recovery of C_2H_4 from refinery off-gases.

2. Experimental work

2.1. Materials and apparatus

CH_4-C_2H_4 gas mixture is supplied by Beijing Bei Temperature Gas Company. The concentration of CH_4 is 47.97 mol%, which are determined by gas chromatograph (Agilent 7890). The uncertainty of the gas compositions is ±0.05 mol%. Analytical-grade TBAB with the purity of 99.0 mol% is from Beijing Modern East Fine Chemicals Ltd. Deionized water with the resistivity of $15 \times 10^6\ \Omega$ cm is prepared by SZ-93 water distillation unit.

The experimental apparatus, as shown in Fig. 1, consists of a hydrate crystallizer, an air bath and a hand pump. The crystallizer has a volume of 420 ml and a design pressure of 20 MPa. The temperature and pressure of the reaction system in the crystallizer were measured by a platinum resistance thermometer with the accuracy of 0.1 K and a pressure sensor with the accuracy of 0.01 MPa, respectively. The temperature window and pressure window in this work are 274.15–285.15 K and 0.30–3.70 MPa, respectively. A magnetic stick was installed inside of the crystallizer to constantly stir the reaction system.

2.2. Methods

First, the formation condition of CH_4-C_2H_4 hydrate in water and 10 wt% TBAB aqueous solution were measured by pressure search method. Then, the equilibrium separation of CH_4-C_2H_4 via hydrate formation was investigated under constant temperature and pressure. The methods and procedures were described in our previous work (Sun et al., 2011a, 2011b, 2012a, 2012b, 2015), which show the good reliability of the apparatus and method.

3. Results and discussion

3.1. Formation condition of CH_4-C_2H_4-TBAB hydrate

Fig. 2 illustrates the formation conditions of CH_4-C_2H_4 hydrate in water and 10 wt% TBAB aqueous solution. It shows that the influence of TBAB on the formation of CH_4-C_2H_4 hydrate changes with the temperature. TBAB performs as a hydrate promoter at low temperature and as a hydrate inhibitor at high temperature. This occurs because TBAB forms semi-clathrate hydrate with water at low temperature, so it can reduce the formation pressure of CH_4-C_2H_4 hydrate as a promoter. However, when the temperature is too high for TBAB to form hydrate, TBAB exists in the water as a kind of salt compound, which inhibits the formation of CH_4-C_2H_4 hydrate. The similar experimental rule, i.e., an inflection point appeared in the phase equilibria diagram, could be also found in our previous work regarding TBAB-synthesized gas system (Liao et al., 2015). The formation temperature for 10 wt% TBAB Type B hydrate is about 280.15 K at atmospheric pressure (Arjmandi et al., 2007). Consequently, when the temperature is higher than 282.15 K in this work, TBAB can not form hydrate even at a pressure near 2 MPa and acts as an inhibitor of CH_4-C_2H_4 hydrate.

3.2. Separation of CH_4-C_2H_4 via hydrate formation with TBAB

The separation results are presented in Tables 1–3. The recovery yield of C_2H_4 (R_2) (Linga et al., 2007a) in the equilibrium gas and the

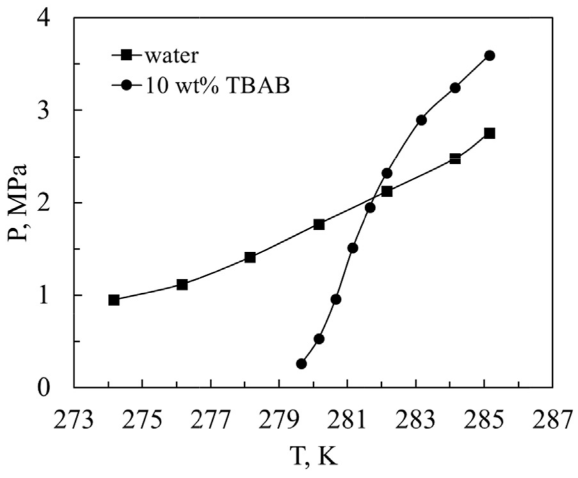

Fig. 2. Formation conditions of 47.97 mol% CH_4-C_2H_4 hydrate in different solutions.

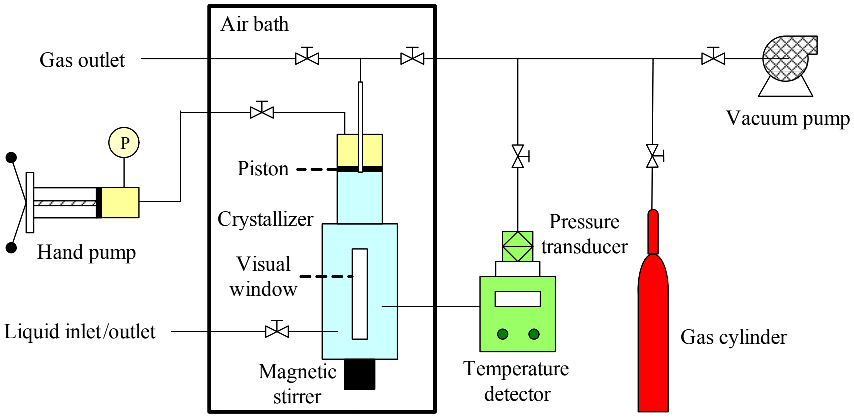

Fig. 1. Schematic sketch of the experimental apparatus.