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Experimental and modeling study on the phase equilibria for hydrates of gas mixtures in TBAB solution

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HIGHLIGHTS

- The hydrate phase equilibria of gas mixture in TBAB aqueous solutions were measured.
- An inflection point in the *P–T* curve of hydrate phase equilibria was found.
- A thermodynamic model was proposed for investigation of gas mixtures+TBAB semiclathrate hydrates.
- Ethylene molecules are supposed unable to occupy the dodecahedral small cages in the TBAB semiclathrate hydrates.
- Hydrate structures transformed from semiclathrate hydrates to pure structure I hydrates.

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ABSTRACT

Accurate calculation of equilibrium formation conditions of hydrates is important for gas storage and separation based on hydrate technology. In this work, the hydrate formation conditions of a synthesized gas mixture in tetra-n-butyl ammonium bromide (TBAB) aqueous solution were measured at temperature ranging from 278.1 to 286.2 K. An inflection point in the *P–T* curve of hydrate phase equilibria was found. It is suggested that the hydrate structures transformed from semiclathrate hydrates to pure structure I hydrates with an increase in formation temperature. Then a thermodynamic model was proposed for calculating formation conditions of the semiclathrate hydrates formed from the gas mixtures+TBAB aqueous solution. The Patel–Teja equation of state was used to calculate the fugacity of gaseous hydrate former and several correlations were used to calculate the properties of TBAB. Ethylene molecules are supposed not to be able to occupy the dodecahedral small cages in the TBAB semiclathrate hydrates under the experimental *P–T* conditions. The presented model results show good agreement with the experimental data and the literature data.

1. Introduction

Clathrate hydrates are crystalline solid compounds formed by guest molecules of gas and host molecules of water under appropriate temperature and pressure conditions. Water molecules link with each other by forming hydrogen bonds and constitute cages around gas molecules. Structure I (sI), structure II (sII) and structure H (sH) are three different structures of clathrate hydrates mostly depending on the size of gas molecules (Sloan and Koh, 2008). Different from conventional clathrate hydrates, semiclathrate ones are composed of quaternary ammonium salts, water and small gas molecules such as CH_4, CO_2, N_2, H_2, etc. Tetra-n-butyl ammonium bromide ($(n\text{-}C_4H_9)_4NBr$, hereafter TBAB) semiclathrate hydrates are regarded as the most commonly used semiclathrate hydrates. In the TBAB semiclathrate hydrates, the cages are formed by physical combination of bromide ions and water molecules linked by hydrogen bonds. The tetra-n-butyl cation ($(n\text{-}C_4H_9)_4N^+$, hereafter TBA^+) occupies four big cages (two tetrakaidecahedra cages and two pentakaidecahedra cages, a part of the cage structure is broken), and the small gas molecules occupy the remaining dodecahedral small cages (Shimada et al., 2005). Because of their increase in gas storage capacity, improved selectivity of the small dodecahedral cavities for trapping the gas molecules, and moderate stability pressure–temperature conditions (Duc et al., 2007; Eslamimanesh et al., 2012a,b; Makino et al., 2010; Mohammadi et al., 2011), the semiclathrate hydrates of TBAB have been widely

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used for gas storage and transportation, separation of gas mixtures and CO_2 sequestration (Gholinezhad et al., 2011; Hao et al., 2008; Kamata et al., 2005).

Different gases require different conditions to form hydrates and the dodecahedral cavities in semiclathrate hydrates have selectivity for trapping small gas molecules. It leads to the difference of the corresponding phase behaviors. Based on these characteristics, several researchers successfully separated gas mixtures by hydrate crystallization in TBAB aqueous solutions. For example, Kamata et al. (2005) removed H_2S from biogas ($CH_4+CO_2+H_2S$) with TBAB semiclathrate hydrates and the recovery of H_2S is more than 90%. Shimada et al. (2003) and Kamata et al. (2004) found that TBAB semiclathrate hydrates can be used to separate small gas molecules which could be incorporated into dodecahedral cages. They succeeded in separating CH_4 from $CH_4+C_3H_8$ or $CH_4+C_2H_6$ gas mixtures. Duc et al. (2007) conducted separation experiments using TBAB as an additive in order to capture CO_2 from a gas mixture by hydrate crystallization. The experimental results showed that the presence of TBAB considerably decreases the formation pressure of simple hydrates (CO_2 or N_2) and mixed hydrates (CO_2–N_2). Sun et al. (2011) systematically studied the separation of CH_4 and N_2 via hydrate formation in a TBAB solution. The recovery of CH_4 is more than 47%. They also found that the hydrate growth rate accelerates greatly with the additive of sodium dodecyl sulfate (SDS) in TBAB solution. Xu et al. (2012, 2013) and Li et al. (2010a,b) conducted thermodynamic and Raman spectroscopic analysis studies on CO_2 separation from CO_2–H_2 gas mixtures via hydrate formation in the presence of TBAB. Nonetheless, there are no literatures focusing on phase equilibria of gas mixtures containing C_2H_4 in TBAB aqueous solutions. C_2H_4 is one of the important compounds in refinery dry gas mixtures. The research on purification of C_2H_4 gas using hydrate crystallization is of great significance.

In order to separate gas mixtures or store gases in the presence of TBAB, there is a demand for accurate and reliable experimental data for relevant TBAB semiclathrate phase equilibria. Several researchers conducted experiments to obtain phase equilibrium data for TBAB semiclathrate hydrates of CH_4, N_2, CO_2, H_2 and H_2S with different fractions of TBAB. Arjmandi et al. (2007) measured the phase boundaries of TBAB and different gases double hydrates such as H_2, CH_4, N_2 and CO_2. The results showed that TBAB semiclathrate hydrates and the studied gases are more stable than conventional sI or sII hydrates at low-pressure conditions. Mohammadi and Richon (2010), Mohammadi et al., (2011) used an isochoric pressure-search method (Belandria et al., 2011a,b; Mohammadi et al., 2008; Ohmura et al., 2004; Tohidi et al., 2000; Tumba et al., 2011) to obtain experimental dissociation data for semiclathrate hydrates of TBAB+H_2S, CH_4, CO_2, N_2, or H_2.

Recently, research on the modeling phase equilibria of semiclathrate hydrate systems has attracted lots of attention. The phase behavior of semiclathrate hydrates is complex and difficult to analyze. Furthermore, some researchers (Shimada et al., 2005; Mohammadi et al., 2011; Duc et al., 2007; Mohammadi et al., 2012a) proved that the structures of semiclathrate hydrates can be changed with increasing/decreasing concentrations of TBAB in aqueous solutions or changing of temperature–pressure conditions. As a result, it makes modeling of phase equilibria of semiclathrate hydrate systems more difficult. Mohammadi et al. (2012b) developed a feed-forward artificial neural network algorithm to estimate the hydrate dissociation conditions for the H_2+water and H_2+TBAB+water systems. Moreover, they proposed a thermodynamic model (Eslamimanesh et al., 2012b; Najibi et al., 2015) on the basis of the vdW-P solid solution theory to estimate the dissociation conditions of TBAB semiclathrate hydrates of CO_2/CH_4/N_2. Nonetheless, the extension of the model they proposed to the multi-component systems needs further study. Liao et al. (2013) developed a modified model to calculate phase equilibria of TBAB semiclathrate hydrates+CH_4, CO_2, N_2 or gas mixtures on the basis of the calculation of sII hydrate in the Chen and Guo model (Chen and Guo, 1998). Fukumoto et al. (2014) used a thermodynamic approach proposed by Paricaud (2011) to determine the dissociation conditions of H_2 semiclathrate hydrates with TBAB, TBAF, TBPB and $TBANO_3$ salts. Good prediction results are obtained over wide ranges of salt concentrations and pressures. Baghban et al. (2015) have developed a Support Vector Machine (SVM) model and coupling of Support Vector Machine with Genetic Algorithm (GA-SVM) model to predict semi-clathrate hydrate pressure of CO_2, CH_4, N_2, H_2, Ar, Xe and H_2S in TBAB aqueous solution. A low parameter connectionist technique was applied to predict phase equilibrium modeling of semi-clathrate hydrates with the fast rate and cheap method of calculation. Verrett et al. (2015) constructed a thermodynamic model by adapting common existing models to semi-clathrate systems. It is successfully used for TBAB–H_2O–CO_2 and TBAB–H_2O–CH_4 semi-clathrate systems in the temperature range of 281–294 K. Compared with the above model, the model presented in this work is more accurate and simplified, especially in the prediction of gas mixture in TBAB aqueous solution. The hydrate formation mechanism is different and the improved calculating temperature range of the model is 276–297 K.

In this work, experimental phase equilibria data of a synthesized gas mixture in semiclathrate hydrates with different concentrations of TBAB in water were obtained using the isochoric pressure search method. The interesting phase behavior was observed, that is the synthesized gas mixture+TBAB hydrate phase equilibrium curve exhibits an inflection point, which is similar to the TBAC+CH_4 hydrate system (Makino et al., 2010). It is suggested that the crystal structure of the synthesized gas mixture+TBAB hydrate system transforms from TBAB semiclathrate hydrates to pure sI hydrates. In addition, a modified thermodynamic model based on the two-step hydrate formation mechanism in the model of (Chen and Guo, 1998), was proposed for calculating phase equilibria of semiclathrate hydrates of the gas mixtures in TBAB aqueous solution. Eventually, it is supposed that C_2H_4 molecule cannot be incorporated into dodecahedral (5^{12}) cages of TBAB semiclathrate hydrates by the experimental and modeling study on the phase equilibria for hydrates of the synthesized gas mixture in TBAB aqueous solution.

2. Experimental work

The composition of the synthesized gas mixture was selected from one oil refinery in China. It was prepared by the Beijing AP Beifen Gas Industry Company and its composition is listed in Table 1. TBAB with analytical purity (99.0%) was supplied by the Shanghai Sinopharm Chemical Reagent Company. The compositions of the feed gas and the gas phase in the reactor were measured by a gas chromatograph (HP7890).

To estimate the temperature and pressure of the experiment, the Chen–Guo hydrate model (Chen and Guo, 1998) was used to calculate the hydrate formation conditions of the experimental gas in pure water and the results are shown in Table 2.

2.1. Experimental apparatus

A schematic sketch of the experimental apparatus is shown in Fig. 1. The reactor equipped in an air bath is the same as given in our previous work (Sun et al., 2011). The reactor is made by

Table 1
Molar composition of feed gas mixture.

Components	CH_4	C_2H_6	C_2H_4	CO_2	H_2
Composition (mol%)	15.90	4.95	53.13	0.92	25.1