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Separation of methane–ethane gas mixtures via gas hydrate formation

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ABSTRACT

In this study, a new technique to separate methane–ethane binary mixtures via gas hydrate formation has been developed. The experimental data of mixed methane–ethane gas hydrate formation have been studied at various compositions of mixture (0.1, 0.2, 0.3, 0.5, 0.68, 0.8 and 0.9 mol fractions of methane). In order to determine the composition of gas during hydrate formation, an algorithm has been introduced based on Langmuir adsorption model. This algorithm can discuss with regard to the system behavior during mixed gas hydrate formation at various mole fractions of methane and ethane; for example it explains how the hydrate formation process becomes 2 stages at low mole fractions of methane. The results show that two gases were fully separated at low and high mole fractions of methane in the mixture.

1. Introduction

Gas hydrates are crystalline and ice-like compounds in which individual guest molecules are caged inside a network of water molecules. Gas hydrates can be formed at low temperatures close to the freezing point of water and at high pressure of experimental condition [1]. The study on gas hydrate formation is significant because of new scientific fields such as the development of hydrate-based technologies including gas separation, gas storage, CO_2 sequestration and prevention of gas hydrate hazards [2,3].

Hydrate formation from gas mixture mainly depends on the gas composition. Small molecules such as pure methane, ethane and carbon dioxide form structure I of hydrates while larger molecules such as propane only form structure II of hydrates. In the case of mixtures, the structure is not always distinguishable, a priori. For example, while pure methane and pure ethane are only thermodynamically form structure I hydrates, it has been observed that mixtures of the two components may also form structure II hydrate [4,5]. In the case of a gas mixture that propane is present, it has been observed that only a small amount of propane is required to form structure II hydrate. Inasmuch the physical properties of sI and sII hydrates are different, and the thermodynamics and the kinetics are also expected to be different [6,7].

Adamova et al. performed calculations of phase transformations structure sI-structure sII for binary methane–ethane hydrates in the framework of molecular level model. They determined the conditions of hydrate formation in equilibrium with gas phase and ice at different gas phase compositions and pressures. They have shown that even at very low ethane concentration in the gas phase (about 0.5%) hydrate structure sII becomes more stable than sI. Also they predicted regions of stability in T, P plane of sI and sII structure for mixed hydrate [8].

Chen et al. measured phase equilibrium conditions of pure and mixed gas hydrate in several systems by the step-heating. For gas mixture system, the composition of gas phase analyzed by gas chromatogram at the end of each equilibrium stage was assumed as the equilibrium composition at the equilibrium pressure and temperature. They found that this method exactly fits the meaning of “phase equilibrium” [9].

Luo et al. developed a new technique for separating gas mixtures via hydrate formation by means of a set of medium sized experimental bubble column reactor equipment that the liquid phase was in the axial dispersion regime and the gas phase was in the plug flow regime. They simulated the rate of hydrogen enrichment for $CH_4 + H_2$ gas mixtures in the presence of hydrate promoter THF [10].

Nagata et al. compared two types of gas separation methods, using liquefaction and gas hydrate formation, in terms of the equilibrium recovery ratio for the separation of gaseous mixtures of HFC-134a and nitrogen. They found that more HFC-134a can be recovered by the hydrate-based separation than the liquefaction separation method [11]. Sun et al. studied gas mixtures separation efficiency via forming hydrate. The separation efficiency was examined for hydrogen + methane gas mixtures in pure water, 1

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Nomenclature

A	constant for calculating Langmuir constant
B	constant for calculating Langmuir constant
C	langmuir constant
f	gas fugacity
n	number of moles of gas that occupied the cavities
n_w	hydrate number
P	pressure
r	gases ratio in hydrate phase
R	universal gas constant
T	temperature
V	volume
y	mole fraction
Z	compressibility factor
Greek letters	
ν	number of cavities per molecules of water
θ	fractional filling of cavities
Δ	different operator
φ	fugacity coefficient
Subscripts	
c	cavity type
i	gas component
j	time denotation
m	total number of gas components
w	water
Superscripts	
g	gas

and 6 mol% THF in initial aqueous solution. They found that high operation pressure is needed for separation from pure water, while with existence of THF in aqueous solution hydrogen was remarkably enriched in vapor phase [12].

Zhang et al. investigated experimentally the vapor-hydrate equilibria for $CH_4 + C_2H_4$ + THF + water systems. Their results demonstrated that, because of the presence of THF, ethylene was remarkably enriched in vapor phase instead of being enriched of in hydrate phase for $CH_4 + C_2H_4$ + water system [13]. Wang et al. analyzed the key problem in CO_2 capture from the different sources such as shifted synthesis gas, flue gas and sour natural gas or biogas. They also explored the possibility of separating different gases by selective hydrate formation and reviewed the progress of CO_2 separation from shifted synthesis gas, flue gas and sour natural gas or biogas [14].

In the current work methane–ethane mixed hydrate formation has been studied experimentally and theoretically and a new technique for the separation of two gases has been developed by using gas hydrate formation. In this study, Langmuir adsorption model has been used to determine the composition of gas phase during methane–ethane mixed hydrate formation process.

2. Apparatus and procedure

2.1. Apparatus

The experimental data of hydrate formation for methane–ethane gas mixtures at various mole fractions of methane and ethane have been obtained by using an experimental setup. The schematic of setup is shown in Fig. 1. The reactor is a stirred batch reactor with the volume of 500 cm^3, which is capable at operating pressures range of 0–100 bars. It was equipped with a jacket for the heating and cooling of system; so the temperature of reactor was controlled by circulating a coolant. Setup includes cooling bath, heating electric, vacuum pump and two separate reservoirs for gas and liquid storage. The temperature was measured using PT100 thermometers with an accuracy of ±0.1 K. The cell pressure was measured using a digital barometer with an accuracy of about ±0.1 Mpa. The signals of pressure and temperature were acquired by using a data acquisition system driven by a personal computer. The cell pressure and temperature data from the acquisition system were saved at specified sampling intervals on the computer hard disk.

2.2. Procedure

Methane and ethane with a normal purity of 99.5%, supplied by a technical gas service, and distilled water have been used. At first, the gas mixtures with experimental fraction of methane/ethane were supplied at the storage cylinder. The hydrate formation reactor was evacuated. Subsequently, 300 cm^3 of distilled water was charged to the reactor. The reactor pressurized to about 0.05 Mpa below the equilibrium pressure for the hydrate formation at the specified experimental temperature. The constant temperature bath was turned on and the reactor was allowed to reach the constant experimental temperature. When the solution attained thermal equilibrium, the reactor was pressurized to the experimental pressure by supplying gas from the cylinder. Mixing was started and data collection began. The present experiments were performed at a speed stirrer of 800 rpm and temperature of 277.15 K. It should be mentioned that the gas/liquid ratio is considered to be 2/3 in every experiment.

2.2.1. Design of experiment

The pure methane and pure ethane both form sI hydrates, but the mixtures of $CH_4–C_2H_6$ may form sI, sII hydrates or both of them, which depends on mole fraction of CH4 in the mixture [15]. As shown in Fig. 2 diagram, pure methane and pure ethane form sI hydrates in the presence of water at pressures of 39.53 and 7.89 bar, respectively. Between the compositions of 0.74 and 0.994 mol fraction methane, sII hydrates form at the incipient formation pressure. These predictions have been confirmed by means of Raman and NMR spectroscopy [15]. If only small amount of ethane added to pure methane will form sII hydrate. So different experimental points have been selected that they correlate with mixtures at 0.1, 0.2, 0.3, 0.5, 0.68, 0.8 and 0.9 mol fractions methane and at pressure of about 36 bar, because in these points the mixtures of 0.1, 0.2 and 0.3 of methane initially form sI hydrates, the mixtures of 0.68, 0.8 and 0.9 of methane initially form sII hydrates and the mixture of 0.5 of methane initially form simultaneous sI and sII hydrates [16].

3. Theory

The mole fraction of CH_4 changes by decreasing pressure during hydrate formation. So it can be calculated by an algorithm based on Langmuir adsorption model with time [17]. In this method, there are two kinds of equilibrium existing during the hydrate forma-