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Hydrate phase equilibrium of binary guest-mixtures containing CO_2 and N_2 in various systems

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ABSTRACT

For sequestration or separation of CO_2 from flue gas, hydrate phase equilibrium of $(CO_2 + N_2)$ binary guest-mixtures (x_{CO_2} = 0.101, 0.180, 0.251 M fraction) was investigated using isochoric multi-step heating dissociation method in various systems, i.e., pure water, Tetrahydrofuran (THF, y_{THF} = 0.004, 0.012, 0.042 M fraction) aqueous solution, Tetrabutyl ammonium bromide (TBAB, y_{TBAB} = 0.004, 0.012, 0.042 M fraction) aqueous solution, natural seawater, seasand and (seawater + seasand) mixture. All measurements were carried out in a temperature and pressure region of (271.5 to 289.6) K and (0.62 to 18.27) MPa, respectively. The results show that the formation pressure of $(CO_2 + N_2)$ hydrate is still too high in pure water, but it can be obviously decreased in TBAB and THF aqueous solution and the pressure drop caused by TBAB is greater than THF only at the lower concentration of solution (in the concentration ranges investigated in this work). In seawater, hydrate formation pressure is raised while the seasand sample has no impact on it. Besides, hydrate equilibrium is mainly influenced by the ions in the (seasand + seawater) mixture while the effect of seasand particles is not obvious.

1. Introduction

Due to the ever-increasing CO_2 emission from flue gas, efficient separation and recovery of CO_2 become a global consensus. Gas hydrates are ice-like clathrate crystalline compounds formed by water molecules and gas molecules under high-pressure and low-temperature condition. Because of its huge gas storage capacity, hydrate-based separation technology has been regarded as a promising way to alleviate the problem of CO_2 emission [1–37]. Glew et al. [27] earlier proposed gas mixture separation utilizing hydrate method and successfully obtained propane and propylene from the mixtures. Since then, the researches on hydrate-based separation were reported continually. CO_2 separation from flue gas through hydrate-based technology is based on the preferential enclathration of molecules due to molecule size and chemical affinity in hydrate structure when hydrate crystals are formed from guest mixtures containing CO_2. Hydrate phase is enriched in CO_2 while other gases are concentrated in vapor phase [1,2,29]. Then CO_2 can be partitioned from the mixtures after hydrate dissociation.

The main components of flue gas from power plant are CO_2 and N_2, the molar fraction of which CO_2 is usually 0.15 to 0.20. Since the formation condition of O_2 hydrate is nearly similar with N_2 hydrate, flue gas can be treated as the binary mixtures of CO_2 and N_2 during experiments [29]. In order to design the separation process, more phase equilibrium data of $(CO_2 + N_2)$ hydrate are required although there are some data. Phase behavior of $(CO_2 + N_2)$ hydrate differs from that of single N_2 or CO_2 hydrate. The equilibrium curve of $(CO_2 + N_2)$ hydrate lies between the curves of CO_2 hydrate and N_2 hydrate. Moreover, $(CO_2 + N_2)$ hydrate can be formed more easily in the presence of a larger molar fraction of CO_2 in binary mixtures [3–6,28,38–41]. As mentioned above, flue gas mainly consists of N_2 so that a relatively high pressure for hydrate formation is required in the presence of pure water, which indicates a huge energy consumption during separation. Therefore, it is necessary to find suitable additives to decrease formation pressure or increase formation temperature. Tetrahydrofuran (THF) and Tetrabutyl ammonium bromide (TBAB) are

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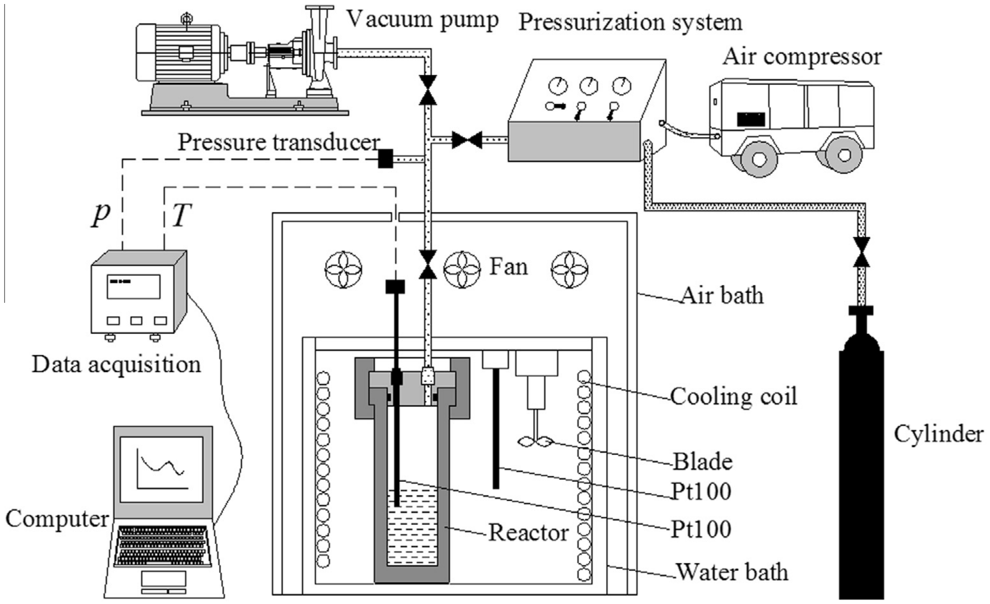

FIGURE 1. Experimental setup for hydrate dissociation conditions measurement [57,61].

two excellent hydrate promoters that have been proposed for CO_2 separation in recent years. Even a small amount of THF or TBAB is able to allow hydrate to form at more favorable conditions [2,3–9,42–50] that greatly reduces the cost of separation. Although there are some phase equilibrium data on $(CO_2 + N_2 + TBAB)$ hydrate and $(CO_2 + N_2 + THF)$ hydrate [2,3–5,42,45,46], those data are not enough for CO_2 separation. In addition, the concentration ranges of TBAB and THF solutions studied in literatures are also relatively narrow and the promoting effects on hydrate equilibrium still need to be investigated and compared.

Recently, it has been proposed that CO_2 ocean disposal is the promising option for alleviating greenhouse effect. When flue gas from power plant is directly injected in marine sediments through pipelines, the gas is accumulated beneath the ocean floor in the form of solid hydrate. The formed hydrate simultaneously helps to generates the caprock and gas-trap space for sequestration. Additionally, the hydrate layer is isolated from the atmosphere by seawater column. So CO_2 ocean sequestration has a higher security relative to inland geological storage [51]. Once CO_2 hydrate dissociation occurs, the escape of large amount of CO_2 gas can be prevented through the multi-trapping mechanism including gravity, hydrate layer, seawater column, other geological or chemistry process etc. Phase equilibrium of hydrate bearing marine sediment can be affected by sediment particles and the ions containing in pore water. Generally, ions can inhibit hydrate formation and reduce hydrate stability zone [37,52–57]. The influence of sediment on the equilibrium depends on solid particle size. In the presence of fine-grained sediment, hydrate equilibrium condition shifts to low temperature region, nevertheless, no change occurs in coarse-grained sediment [58–63]. In order to undertake the ocean disposal of flue gas, phase equilibrium of $(CO_2 + N_2)$ hydrate in marine environment should be understood in the first place. Unfortunately, the equilibrium data in the presence of seawater and sediments have not been reported.

In this work, hydrate phase equilibrium of $(CO_2 + N_2)$ binary mixtures containing different molar fraction of CO_2 were investigated in various systems (pure water, THF/TBAB aqueous solution, seawater, seasand and the mixtures of seawater and seasand) to provide important data for CO_2 separation and sequestration.

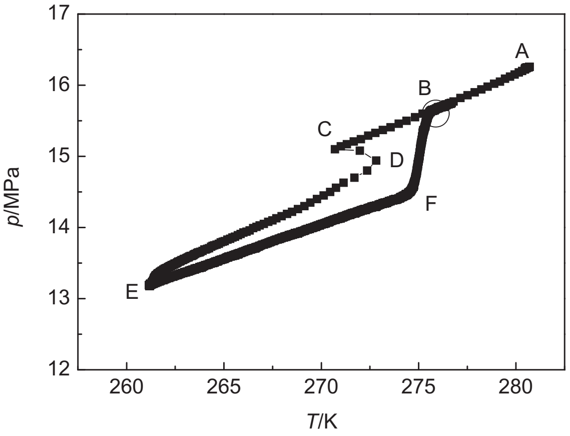

FIGURE 2. A typical isochoric p–T curve of hydrate formation and dissociation.

2. Experimental

2.1. Experimental equipment and procedure

An experimental setup was built for the measurement of gas hydrate equilibrium, which consisted of hydrate reactor, temperature-controlled system, data acquisition system, and gas supply system, as shown in figure 1 [57,61]. The pressure and temperature during the experiments were detected by a pressure transducer (with an uncertainty of ±0.02 MPa) and platinum resistance thermometer sensor (with an uncertainty of ±0.1 K), respectively. The isochoric multi-step heating dissociation method was used to determine the hydrate phase equilibrium because it had a higher accuracy than other methods [59–64]. The typical isochoric p–T curve of hydrate formation and dissociation is shown in figure 2. After the hydrate vessel was evacuated, the deionized water/aqueous solution and gas mixture were injected into it. At this time, the temperature and pressure was far away from the hydrate nucleation region. Then the system was left overnight for the gas sufficiently dissolving and saturating in the medium. After the temperature and pressure stability, the temperature was slowly