



Effect of graphite nanoparticles on CO₂ hydrate phase equilibrium



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ABSTRACT

Stepwise heating method was used to determine the hydrate phase equilibrium in the water containing graphite nanoparticles. The results show that, compared with deionized water at a given temperature, a significant upward shift of the formation pressure of the CO₂ hydrate formed in graphite nanoparticles suspensions was observed, but the phase equilibrium curves of CO₂ hydrate formation in the different graphite nanoparticles concentrations were basically consistent. In this regard, graphite nanoparticles have a negative effect on the gas hydrate formation. In addition, an improved hydrate thermodynamic model was proposed to predict the hydrate equilibrium conditions under the system of graphite nanoparticles suspensions. The results show that the maximum average deviation of pressure predicted by model is 3.39, but the minimum average deviation is 2.21. It indicates that the data of the model prediction was good agreements with the data obtained from experiments.

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1. Introduction

Gas hydrates are defined as compounds in which gas molecules are trapped in a host lattice formed by water molecules [1]. Nowadays, a series of new technologies had been developed under the basis of its excellent physical and chemical properties, including carbon capture and storage (CCS) [2], natural gas storage and transportation [3], seawater desalination [4] and so on. With respect to these technologies, good prospects in their respective fields are expected in the future, especially for CCS. Currently, the main reason contribute to the aggravation of the global warming effect is the excessive emissions of CO₂ gases, so CCS have become the focus of global attention. Four conventional processes were applied to remove CO₂ from some of the gas mixture. i.e. chemical adsorption [5], physical adsorption [6], separation via membranes [7] and cryogenic fractionation [8]. However, these methods suffer from limitations such as large energy consumption, high costs, low efficiency and ungreen. Gas hydrate provides a new method for CCS and was considering being a low investment, high efficiency and

environment-friendly way to solve the problem of global warming [2]. Whereas, in order to industrialize this technology, the rate of gas hydrate formation and storage capacity should be increased.

Generally, stirring [9], bubbling [10], spraying [11] and adding surfactants [12] can be used to accelerate the rate of hydrate formation and enlarge its storage capacity. As argued recently by Link [13], Adding surfactants are more safe and low-cost than other methods. However, a special additive, can greatly improve the heat and mass transfer of hydrate formation system, is the key of this method. Nanofluids, as a new type of hydrate additive, was reported by Li [14] in the literature for the first time. Then, Park [15] proved that carbon nanotubes can reduce the induction time of hydrate formation and improve its storage capacity. Mohammadi [16] reported that an appropriate amount of SDS mixed with silver nanoparticles can greatly enhance the rate of hydrate formation. Synthesized silver nanoparticles were applied to promote hydrate formation by Arjang [17] recently. In addition, Govindaraj [18] and Haghtalab [19] also obtained the same conclusions that nanofluids had a positive effect on hydrate formation. Obviously, all of nanoparticles mentioned above are metals and oxides which cannot withstand the acidic conditions (PH < 7). However, it is certain that the industrial application of the hydrate technologies will always occur under an acidic environment. For this reason, an acidic-resistant material such as metalloid is an ideal additive to promote hydrate formation [20]. Therefore, graphite nanoparticles,

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with a high thermal conductivity in metalloid, were used to promote CO₂ hydrate formation by ZHOU [20] recently. The results showed that the induction time of hydrate formation decreased, while the hydrate storage capacity increased.

Hydrate formation needs the proper temperature and pressure conditions. However, the calculation of stable condition for the thermodynamic equilibrium is the basis of determining the critical temperature and the critical pressure [21]. So, determine the phase equilibrium and establish relevant thermodynamic model is important for hydrate research. At present, the phase equilibrium of hydrate formation in water containing nanoparticles was hardly discussed in the literature. This work adopted stepwise heating method to determine the hydrate phase equilibrium. Besides, an improved hydrate thermodynamic model, based on the traditional model of van der Waals and Platteeuw [22], was proposed to predict the hydrate phase equilibrium conditions in the water containing graphite nanoparticles. The results may indicate the direction of the development of more effective promoters.

2. Experimental

2.1. Materials

Sodium dodecyl sulfate (SDS) with a purity of 99% was obtained from Hubei Dixin Chemical Manufacturing Co., Ltd. (China). A concentration of 99.9% graphite nanoparticles was purchased from Xuzhou Jiechuang New Material Technology Co., Ltd. (China) and its particle average fineness is 50 nm. A purity of 99.8% carbon dioxide was acquired from Changzhou Jinghua Industrial Gases Co., Ltd. (China). Deionized water and distilled water was prepared in the laboratory, and all the indicators agree with industry standards. In addition, an accurate balance with an accuracy of ± 0.0002 g was used in aqueous solutions preparation.

2.2. Apparatus

Fig. 1 shows the schematic diagram of the experimental apparatus. Overall, five units had been incorporated into the system. i.e. air intake system, liquid feeding system, optical imaging system, refrigeration system and digital data acquisition system. CO₂, coming from gas cylinder, was fed into the reactor under the action of the compressor. Aqueous solutions were pumped into the reactor by a centrifugal pump. The reactor was equipped with a SS-316 round vessel which can withstand a pressure of 30 MPa and the volume is 500 mL. An agitator, with a speed range of 0–1000 rpm, was installed in the reactor. It was used to mix the CO₂ and aqueous solutions. In addition, a precision of ± 0.1 K (253.15–293.15 K)

thermocouple (Pt 100) was installed to measure the temperature in the reactor. The pressure in the reactor was measured by a BD pressure transducer (0–10 MPa). The sensor was purchased from BD sensors Co., Ltd. (Germany). A suction pump was equipped to remove the gas inside the reactor. The core unit of the refrigeration system is a thermostat (258.15–268.15 K) which was used to cool the hydrate formation system. Data of the temperature and pressure were tracked and recorded at 1 s intervals by a digital data acquisition system.

3. Theory and methods to determine phase equilibria

3.1. Theoretical background

Stepwise heating method was employed to determine the hydrate phase equilibrium data, which had been reported in the literature by Torre [23], Zhang [24], Sangwai [25] and Shi [26] respectively. Two steps were included in the method. Step 1, Hydrate formation in isochoric reactor by means of cooling. Step 2, Hydrate dissociation in the reactor by increasing temperature gradually. Both of the data obtained in the process of hydrate formation and dissociation were used to plot P–T curve. One typical P–T curve for CO₂ hydrate formation in graphite nanoparticles suspensions was shown in Fig. 2. At first, the pressure dropped gradually by reducing the temperature (A–C). Then, hydrate crystal nuclei appeared (C–D). Next, mechanical agitator was turned on to

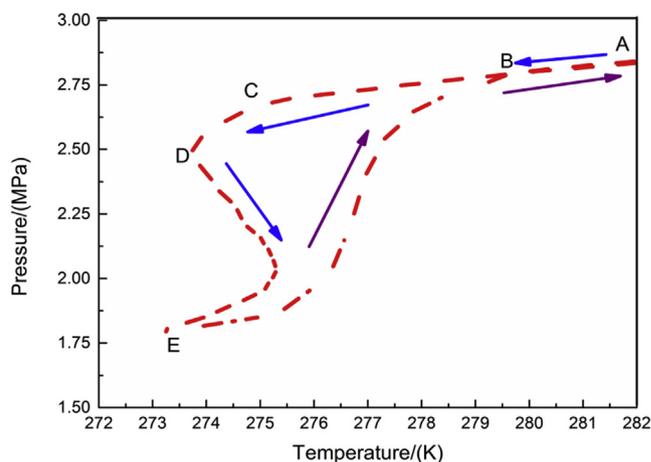


Fig. 2. Typical P–T curve for CO₂ hydrate formation in graphite nanoparticles suspensions.

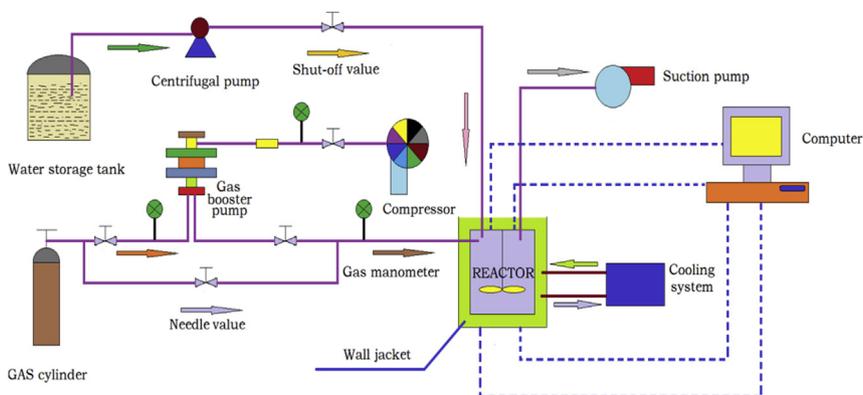


Fig. 1. Schematic diagram of the experimental apparatus.

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