



Solubility of CO₂ in water and NaCl solution in equilibrium with hydrate. Part I: Experimental measurement



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ABSTRACT

In this work, the formation conditions of CO₂ hydrate in different solutions were measured and calculated by the Chen–Guo hydrate model. Then, the solubility of CO₂ in water in equilibrium with hydrate were determined and compared with reference data. The good agreement between the experimental and reference values demonstrates the reliability of the apparatus and method in this work. Finally, we measured the solubility of CO₂ in 1.0 wt%, 3.0 wt% and 3.6 wt% NaCl solutions in equilibrium with hydrate under near temperature and pressure conditions of seabed. The influences of temperature, pressure and NaCl concentration on the solubility of CO₂ were also investigated. The results show that the solubility of CO₂ in NaCl solution is less than that in water. It increases with the temperature, and decreases with the pressure and concentration of NaCl.

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1. Introduction

The greenhouse effect resulting from the emission of greenhouse gases brings about severe worldwide temperature increase and climate abnormality. The global average temperature has increased by 0.3–0.7 °C in the past century, and it may increase by about 3 °C at the end of 21st century without effective control of the greenhouse effect [1,2]. It is known to all that CO₂ is the main contributor to the greenhouse effect with a proportion of about 80% among the greenhouse gases [3]. Consequently, the capture and storage of CO₂ has attracted great research attention in the past decades [4–8]. Undersea storage of CO₂ in the form of hydrate is believed as one of the feasible method [9]. Hydrate is a kind of cage-like compound formed by gas and water at certain temperature and pressure [10,11]. In hydrate, water molecules form cages by hydrogen bond. Gas molecules are encased in the cages by van der Waals force to make the hydrate stable [10,11]. Hydrate has a huge gas storage capacity as one unit volume of hydrate could contain 160–180 unit volume of gas [12–14]. CO₂ forms hydrate relatively easily. The formation pressure of CO₂ hydrate is between 1.2 and 2.0 MPa with the temperature window of 0–4 °C [15,16]. Therefore, the undersea condition is suitable for the stable existence of CO₂

hydrate. In sum, undersea storage of CO₂ in the form of hydrate is an effective approach of CO₂ sequestration with good prospect.

The solubility of CO₂ in seawater concerns the stability of CO₂ hydrate and the change of marine environment. However, solubility data of CO₂ in pure water in the presence of gas hydrate are limited [17–19]. Consequently, solubility of CO₂ in NaCl solution in the equilibrium with hydrate has been investigated in this work.

2. Experimental

2.1. Materials and apparatus

The sources and specifications of the experimental materials are presented in Table 1. Fig. 1 shows the schematic sketch of the experimental apparatus, which was described in our previous work [20–22]. It consists of a hydrate crystallizer, an air bath, a hand pump, and a measuring system of the solubility of CO₂ in liquid, which is shown in Fig. 2. Specially, a sieve was installed between the crystallizer and the solubility measuring system to keep CO₂ hydrate from flowing out of the crystallizer.

2.2. Methods

The methods [23] for measurement of the solubility of gas in liquid generally include bubble point pressure method, calculation method of PVT properties of gases, and displacement method of the

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Table 1
Specifications of experimental gases and reagents.

Materials	Purity	Suppliers
CO ₂	99.99 mol%	Beijing Bei Temperature gas factory
NaCl	≥99.5 wt%	Beijing Shuanghuan chemical reagent factory
NaHCO ₃	≥99.5 wt%	Beijing Shuanghuan chemical reagent factory
Deionized water	15 × 10 ⁶ Ω cm	SZ-93 water distillation unit

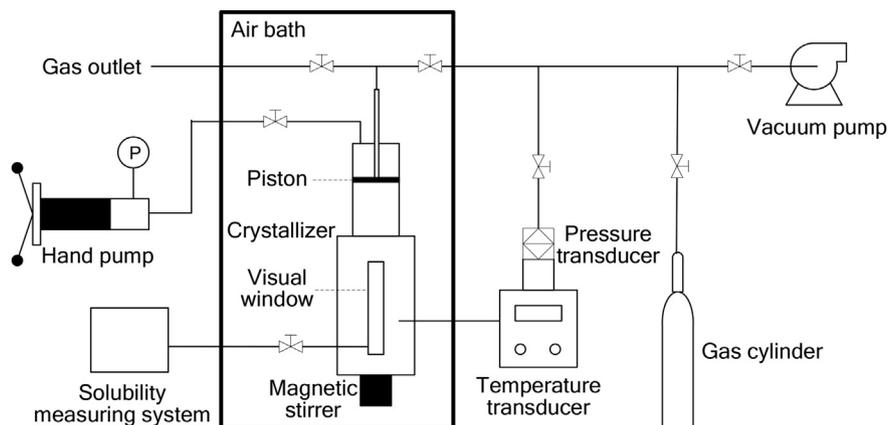


Fig. 1. Schematic sketch of the experimental apparatus.

equilibrium liquid. The displacement method was used in this work to measure the solubility of CO₂ in NaCl solution in equilibrium with hydrate. First, an appropriate amount of NaCl solution was added into the crystallizer, and the air bath was immediately turned on to supply the crystallizer with a constant experimental temperature. Then, CO₂ gas was introduced into the crystallizer until the pressure reached the desired value, and CO₂ began to form hydrate under the stirring action. The pressure should be kept constant by rotating the hand pump during the whole process. If the pressure does not change in 4 h, the reaction system could be regarded to achieve a gas–liquid–hydrate three-phase equilibrium state. Finally, the liquid was carefully transferred out of the crystallizer to the solubility measuring system under the constant experimental pressure. The volume of the displacement liquid was measured and the solubility of CO₂ was calculated accordingly.

3. Calculation

3.1. Solubility of CO₂ in water in equilibrium with hydrate

The calculation of solubility of CO₂ in water is used the method

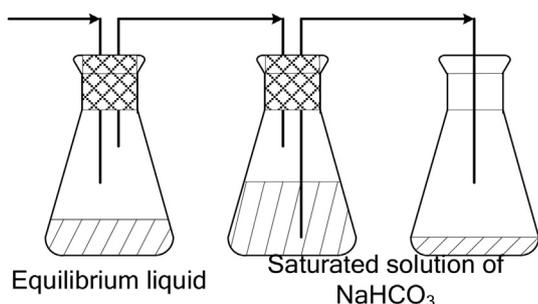


Fig. 2. The measuring system of the solubility of CO₂ in liquid.

of Someya et al. [17]. After the atmospheric flash in the solubility measuring system, the displacement volume of NaHCO₃, i.e., the volume of the released CO₂ (V_g) from water, was obtained first. However, a small part of CO₂ still dissolved in the water. The quantity of the dissolved CO₂ is calculated using Henry's law, and the Henry's law constant of CO₂ (H) is from the reference data [24,25]. Consequently, the solubility of CO₂ (S) is calculated as follows:

$$m = n_c M_c + n_w M_w \quad (1)$$

$$n_c = \frac{P_c V_g}{RT} + n_w \frac{P_c}{H} \quad (2)$$

$$n_w = \frac{m - M_c \frac{P_c V_g}{RT}}{M_w + \frac{P_c}{H} M_c} \quad (3)$$

$$S = \frac{n_c}{n_c + n_w} \quad (4)$$

where m is the total weight of the equilibrium liquid before atmospheric flash. n is the number of moles. M is the molar mass. Subscript c and w stand for CO₂ and water, respectively. P_c is the pressure of CO₂ in the vapor phase. It should be noted that the compressibility factor and fugacity coefficient of CO₂ are both regarded as 1 in the calculation, because the flash process is carried out at atmospheric pressure. The saturated vapor pressure of water is neglected in the calculation. Consequently, P_c is numeric equivalent of the fugacity of CO₂, i.e., atmospheric pressure in this work. T is the temperature of the flash. R is gas constant, with a value of 8.3145 J/(mol K).

3.2. Solubility of CO₂ in NaCl solution in equilibrium with hydrate

The influences of salting-out constant and ionic strength should be considered in the calculation of NaCl system. The solubility of

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