



Effects of cyclopentane on CO₂ hydrate formation and dissociation as a co-guest molecule for desalination



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ABSTRACT

Cyclopentane (CP) is considered to be a potential co-guest molecule in carbon dioxide (CO₂) hydrate-based desalination. The experimental thermodynamic data of CO₂-CP hydrates were measured for a salt solution, where CP was chosen as a hydrate promoter. Seven experimental cases (62 cycles) were studied with different molar ratios of CP/water (0, 0.0025, 0.005, 0.0075, 0.01, 0.02, and 0.03). Hydrate phase equilibrium data were generated using an isochoric method, and the hydrate saturations were calculated based on gas uptake. The results indicated that the increase in CP concentration significantly decreased the CO₂ hydrate equilibrium pressure to a certain limit; the hydrate saturation also decreased during this process. Also, it was determined that CP encouraged the formation of s-II double CO₂-CP hydrates, which are different from s-I simple CO₂ hydrate. The CO₂-CP guest provides a strengthened stability and moderate hydrate phase equilibrium conditions for hydrate-based desalination. The recommended optimal molar ratio of CP is 0.01 when the increase in equilibrium was more than 10 K, and the decrease in hydrate saturation was less than 2%.

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1. Introduction

Clathrate hydrates are solid compounds in which water molecules are linked through hydrogen bonding and create cavities to enclose a large variety of guest molecules [1]. CO₂ hydrate is known to form a structure I (s-I) hydrate, which is composed of two pentagonal dodecahedra (5¹²) and six tetrakaidecahedra (5¹²6²) cages. Because the concentration of CO₂ has gradually increased and reached a high level in today's atmosphere, which has led to significant climate change and is responsible for approximately 64% of the enhanced "greenhouse effect", the disposal of CO₂ has become an issue of worldwide concern [2,3]. One of the proposed schemes of mitigating CO₂ emission is to sequester it as gas hydrates in ocean and marine sediments [4–6]. The principle of capturing CO₂ is that CO₂ molecules are enclathrated into hydrate cages formed by water molecules [7,8]. Thus, many studies of CO₂ hydrate have been performed regarding the separation of a CO₂-containing gas mixture [9,10]. The hydrate equilibrium conditions for CO₂ capture from a flue or fuel as CO₂ hydrate have been widely investigated [11–13]. There are also studies of the CO₂ hydrate phase equilibrium in water with different salts [14–17], which provide basic information for the development of hydrate-based desalination.

The guest component of a hydrate is critical for hydrate-based technologies and also affects the efficiency, safety and energy consumption of hydrate-based desalination technology. Additives are often used to mitigate the hydrate formation pressure and improve the hydrate formation rate and gas capacity [18–21]. The most common hydrate formation promoters are tetrahydrofuran (THF) [19], tetra-butyl ammonium bromide (TBAB) [22], and sodium dodecyl sulphate (SDS); however, their solubilities in water cannot be ignored particularly for hydrate-based desalination [23–25]. CP is another good promoter and is similarly immiscible with water. Additionally, its promotion effect on hydrates was reported to be larger than that of THF [26]. Corak et al. suggested that the formation of a simple CP hydrate could be used for seawater desalination [27]. Cha et al. [28] also investigated CP hydrates that were formed with co-guest CO₂ molecules at elevated temperatures for the desalination of water with high salinity. However, the equilibrium data of CO₂ hydrate in the presence of CP in a saline solution are limited [29–32]. Recently, Ngema et al. [33] conducted experimental measurements and thermodynamic modelling of the dissociation condition of CP-CO₂ hydrates in different saline solution. It provided some new methods and data for this topic, and still need to be clarified furtherly. With more favourable hydrate formation conditions, CP hydrate has been considered to be a potential media for H₂ storage and CO₂ separation from pre- and post-combustion gases [34]. Additionally, Li et al. [35] combined CP and TBAB as a mixed promoter to separate CO₂ from IGCC fuel gas to increase

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the gas uptake and separation efficiency. To date, certain studies of the effects of CP hydrate promoters have also been conducted [36–39]; however, useful data of CP-CO₂ hydrate phase equilibrium are still limited.

CP is a potential co-guest for CO₂ hydrate-based desalination. The thermodynamic characteristics of CP-CO₂ hydrate formation and the associated dissociation process must be further clarified, particularly with regard to the hydrate phase equilibrium conditions and saturation. In this study, the phase equilibrium conditions for CO₂ hydrate with CP as the co-guest molecule in porous media were investigated experimentally. The hydrate saturation is calculated based on CO₂ gas uptake to analyse the cost and efficiency of the hydrate formation process. The data obtained in this hydrate investigation is significant for future research in this field of study.

2. Experimental

2.1. Experimental apparatus and materials

The experimental apparatus used in this study is shown in Fig. 1, and detailed illustrations are provided in prior publications [40,41]. A high-pressure-resistant vessel made of 316 stainless steel with a volume of 750 cm³ was used as the hydrate formation and dissociation reactor. Six thermocouples with an accuracy of 0.1 K in a hexagonal distribution and one pressure transducer with an accuracy of ±25 kPa were connected to the vessel. The materials used in these experiments are listed in Table 1. Soda glass BZ-01 (0.105–0.125 mm diameter, As-One Corporation, Japan) with a 34.8% porosity was used as the porous medium, and a seawater solution with a 3% mass fraction was simulated using NaCl. Different molar ratios of CP and seawater solution were configured using a precision balance with a minimum reading of up to one milligram. All of the chemicals in these experiments were used as provided without further purification. De-ionized water was used in all experiments.

Table 1
Property and supplier of materials.

Material	Purity ^a /Composition	Supplier
CO ₂	GC 99.9 mol%	Dalian Special Gases Corporation, China
CP	AR 99.0 mol%	Aladdin Industrial Corporation, China
NaCl	GR 99.5 mol%	Tianjin Kermel Reagent Factory, China
BZ-01	Soda glass	As-One Corporation, Japan

^a Purity analysis methods: GC (Gas chromatography), AR (Analytical reagent) and GR (Guaranteed reagent).

2.2. Experimental method and procedures

The isochoric method was used to measure the hydrate phase equilibrium conditions by maintaining volume (V) as a constant, which indicates that no gas and/or solution was added during the cooling process. The hydrate formation/dissociation process was driven by the change in the vessel temperature. The high-pressure-resistant vessel containing water and CP was pressurized with CO₂ to the designated pressure. During the cooling process, the pressure decreased primarily due to gas contraction and the increased gas solubility upon cooling at constant volume. If hydrates began to form, the temperature increased rapidly due to exothermal hydrate formation. When no pressure change occurred, the vessel was heated to promote hydrate dissociation. The vessel pressure was shown to increase with hydrate dissociation. The hydrate phase equilibrium conditions were detected by measuring the intersection point of the cooling and heating isochores. The measured phase equilibrium conditions were considered to indicate that all hydrates had just become fully dissociated.

Dry soda glass (630 cm³) was packed into the vessel tightly with the prepared solution (3 mass% NaCl solution). The injected solution volume occupied 40% of the pore volume in the porous media; this parameter is called the initial solution saturation of the porous medium in experiments was strictly controlled at this value. It also should be mentioned that the initial porosity of soda glass is 34.8%, and the solution volume occupied 40% of the pore volume, which

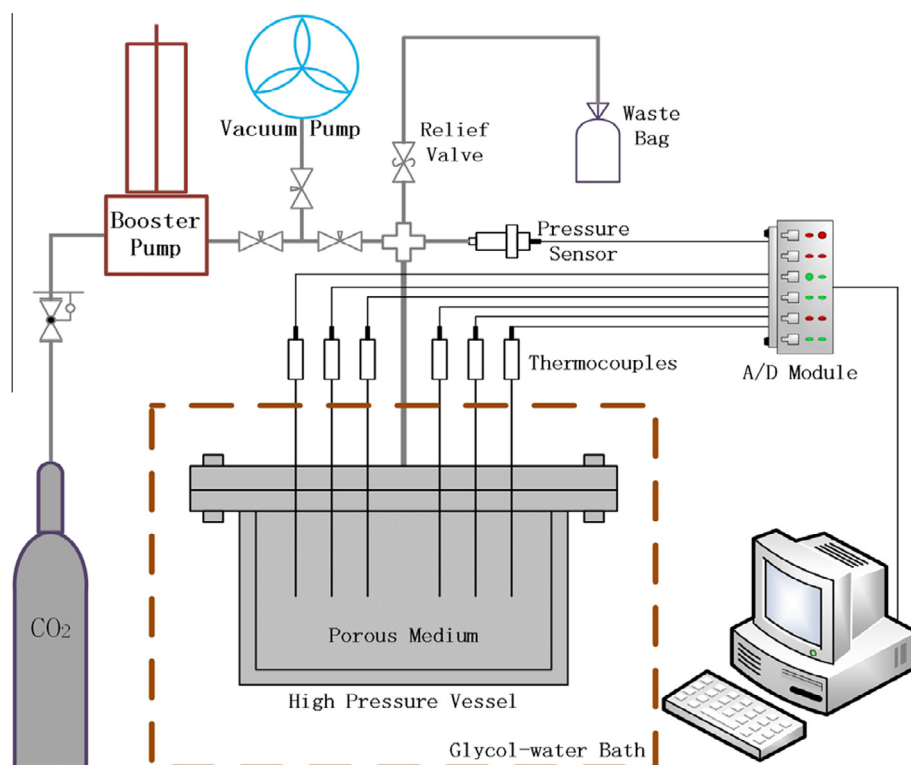


Fig. 1. Schematic of the gas hydrate experimental apparatus.

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