Significance of a thermodynamic promoter (1,3-dioxolane) concentration in promoting CO₂ hydrate: Implication for hydrate-based CO₂ sequestration

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ABSTRACT

Carbon sequestration — is an important method to achieve carbon neutrality and resist climate change. Burying CO₂ in the depth of geological structure and solidifying it into hydrate is a promising carbon sequestration technology. The development of hydratebased CO₂ sequestration requires greater CO₂ storage capacity and mild thermodynamics. In this study, 1,3dioxolane (DIOX) was introduced as the hydrate thermodynamic promoter. The effect of the DIOX-water system lowers than the stoichiometric concentration on the formation of CO₂-DIOX mixed hydrate was evaluated by measuring phase equilibrium and formation kinetics. The results show that DIOX shows thermodynamic promotion to CO₂ enclathration. Even at the ultra-low concentration (0.15 mol%), the system still maintains a phase equilibrium pressure shift of 0.45 MPa. Compared with the system of 5.56 mol%, the system of 3.00 mol% has better formation kinetics; the 0.15 mol% system still maintains considerable CO2 storage capacity (56.0 mmol/mol). The study of low concentration DIOX not only has a practical significance of the passive decline in promoter concentration on large-scale carbon sequestration but also meets the requirements of environmental protection and economy in the use of the thermodynamic promoter. Keywords: CO₂ hydrate, 1,3-dioxolane, Phase equilibria, Kinetics, CO₂ sequestration

NONMENCLATURE

Abbreviations	
APEN	Applied Energy
Symbols	
n	2022

1. INTRODUCTION

Since the industrial revolution, the extensive use of fossil energy has emitted a large amount of CO₂. So far, the CO₂ content of the earth's environment is still increasing net, which is the main cause of climate change, which will lead to a series of environmental problems and even human survival and development [1]. Carbon sequestration is an important way to achieve carbon neutrality through CCS (carbon capture and storage) technology [2]. Hydrate-based CO₂ storage technology is one of the important CCS technology, which can lead CO₂ into the formation depth or depleted waste oil and gas wells with appropriate thermodynamic and pore conditions to form stable CO₂ hydrate [3].

Gas hydrate is a non-stoichiometric cage clathrate, which can wrap small molecular gases (CH₄, CO₂) in water cages with different structures through hydrogen bonds. CO₂ hydrate with high gas storage density (180 v/v) and stability is a good medium for carbon sequestration [4]. Adding thermodynamic promoter (THF, CP) into a CO₂ hydrate system can achieve milder thermodynamics conditions. Thermodynamic promoter molecules occupy the large cage of SII hydrate, so there is an upper stoichiometric concentration limit of the promoter (5.56 mol%) [5]. However, the injection of such a high concentration of the promoter is unfavorable to the environment and the cost is high. For large-scale geological sequestration, high concentration promoters will diffuse in geological water and the concentration will decrease. Therefore, this study focused on the impact of the emerging noncarcinogenic hydrate thermodynamic promoter 1,3dioxolane (DIOX) on the formation of CO₂ hydrate at low concentration (3.00, 0.15 mol%) and analyzed the practical significance of mixed CO₂-DIOX hydrate on CO₂ sequestration in terms of thermodynamics, formation kinetics and storage capacity[6].

2. EXPERIMENTAL SECTION

2.1 Material and methods

CO₂ (99.99 % purity) was purchased from HPT Gas Co., Ltd. 1,3-dioxolane (> 99.8 wt%) was purchased from BEnokai Chemical Co., Ltd. Deionized water was made in the laboratory. 132 mL high-pressure visual reactor, pressure sensor, and thermocouple were used in the experiment. DIOX solution volume is 20 mL. The water bath provides a constant temperature environment for the reactor, and the data acquisition system collects data every 10 s.

The Isovolumetric pressure search method is used in thermodynamic measurement, and the measurement range is 278.0 - 285.0 K [7]. The initial conditions in kinetic measurement are 3.50 MPa and 286.0 K, and sI hydrate will not be formed in thermodynamics. After CO_2 injection and dissolution, it will be cooled to 280.7 K until hydrate is formed.

2.2 Calculation

After the dissolution equilibrium, the Henry constant and CO_2 solubility of the system are recalculated. The gas absorption of the system is:

$$n_t^H = \frac{P_0 V_0}{z_0 R T_0} - \frac{P_t V_t}{z_t R T_t}$$
(1)

$$n_{wt} = n_{w0} - n_t^H \cdot n_H \tag{2}$$

Where the *P*, *T*, *V*, R, and *z* respectively represent the pressure, temperature, gas volume, universal gas constant (8.314 J/(mol·K)), and CO₂ gas compressibility factor (calculated by P-R equation)[8]. Subscripts 0 and t in the formula represent the time when hydrate begins to form and the time in the formation process. n_{w0} and n_{wt} were the initial amounts of water in the system and the amount of water in the reaction process, respectively. n_H is the hydrate number (the number of water molecules consumed by CO₂ molecules), and the theoretical hydrate number of sII hydrate is 5.67 [4]. 5.56, 3.00 and 0.15 mol% DIOX concentration system are 8.5, 6.91 and 5.72 respectively. The normalized Gas uptake rate is (mmol CO₂ / mol aqueous solution):

$$N_G = \frac{n_t^H}{n_{w0}} \tag{3}$$

3. RESULTS AND DISCUSSIONS

3.1 DIOX concentrations on mixed CO₂+DIOX hydrate phase equilibrium



Fig. 1. Measured phase equilibrium *P-T* data of CO₂+DIOX/water system under various DIOX concentrations

1 shows the lower phase equilibrium Fig. measurement results of the CO₂-DIOX solution hydrate three-phase system at the concentration of 0.15, 3.00, and 5.56 mol% DIOX. The black line is the phase equilibrium data of SI CO₂ hydrate of the pure water system from the CSMGem model [9]. The phase equilibrium curves of each DIOX concentration system move towards low pressure and high temperature. Compared with the pure water system, the DIOX system shows the thermodynamic promotion of hydrate. The thermodynamic promotion of the 5.56 mol% and 3.00 mol% DIOX concentration system is strong, and the pressure deviation at 282.5 K is P = 2.23 MPa and 1.74 MPa. Even in the ultra-low concentration 0.15 mol% system, the pressure deviation reaches P = 0.45 MPa. This is still a considerable thermodynamic improvement condition for CO₂ storage in large-scale areas.

3.2 Kinetics measurement





Fig. 2. (a) The gas uptake curves for mixed CO_2 +DIOX hydrate formation under various DIOX concentrations (time zero represents the end of nucleation with error bars showing the standard deviations of two repeated experiments); (b)evolution of morphology of the mixed CO_2 +DIOX hydrates growth process with various DIOX concentrations

Fig. 2 is the gas absorption curve $(CO_2 + DIOX)$ hydrate, solution) of CO₂ during hydrate formation calculated according to equations (1) - (2). After hydrate nucleation, the mixed CO₂-DIOX hydrate in each system grows rapidly, showing a dynamic process from fast to slow. The small picture in Fig. 2 shows the normalized gas uptake rate in t_{30} . When the concentration decreased from 5.56 mol% to 3.00 mol%, the formation kinetics enhanced abnormally. This may be due to the low formation rate of the 5.56 mol% system in the early stage of growth due to the phase separation of DIOX and CO₂ before hydrate nucleation, as shown in Fig. 2b for 0 min. The hydrate formation kinetics of the 0.15 mol% system is weak, and the normalized gas uptake rate is half of the 3mol% system, which is 1.25 mmol/mol/min.

However, at the end of the 170 min hydrate reaction, although the CO_2 storage capacity of the 0.15 mol% system is lower than that of the high concentration system (71.6 mmol/mol), a very considerable storage capacity data (56.0 mmol/mol) is still obtained. The sharp reduction of the concentration does not cause a significant loss of CO_2 storage capacity. This can be explained by the hydrate morphology in Fig. 2b. After the 0.15 mol% system nucleates in the solution, the hydrate crystal shifts to the gas phase direction with stirring, and the hydrate crystal nucleus grows at the gas-liquid interface, which is fully supplemented by CO_2 , while the hydrate of the high

concentration system mainly grows in the liquid phase. Secondly, the tuning effect under a low concentration system makes more large cages occupied by CO_2 , which improves the gas storage potential of the system[13]. The 3.00 mol% system always maintains the flow state in the generation process, which is beneficial to the guarantee of formation fluid flow in the process of CO_2 storage.

As shown in Fig. 3, we compared the amount of CO_2 stored in the hydrate phase and liquid phase and the amount of DIOX used after the reaction in three concentration systems. It can be seen that the storage of solid hydrate is dominant in the storage process. The 5.56 mol% system uses 0.049 mol DIOX to store 0.078 mol CO_2 , while the ultra-low concentration 0.15 mol% system only 0.002 mol DIOX to achieve 0.053 mol CO_2 . It will be very cost-effective in the commercial storage of CO_2 and realize the storage of CO_2 with a low impact on the environment.



Fig. 3. Evolution of (a) CO_2 partition in all phases over time under 4.50 mol% and (b) CO_2 partition ratio at the end of formation process in 0.15 - 5.56 mol% DIOX-water system

CONCLUSIONS

DIOX-water system with a low DIOX concentration (< 5.56mol%) has some advantages in the formation of mixed CO₂-DIOX hydrate. The kinetic performance of the 3.00 mol% system is better than that of the 5.56 mol% system, while the CO₂ storage capacity of the 0.15 mol% system with ultra-low concentration is not seriously damaged compared with that of the higher concentration system. Therefore, the low concentration system meets the requirement of DIOX-water environmental protection and economy and has broad hydrate-based application prospects in CO_2 sequestration in large-scale sites.

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