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Kinetic study of carbon dioxide hydrate formation in presence of silver nanoparticles and SDS

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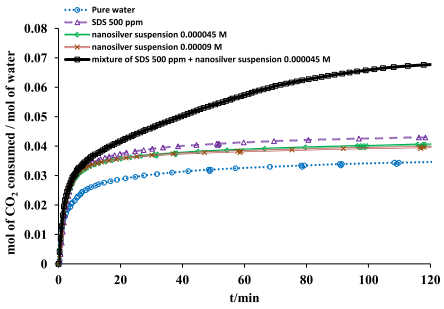
HIGHLIGHTS

- Mixture of SDS + silver nanoparticles increases the storage capacity of CO_2 hydrate.
- Mixture of SDS + silver nanoparticles increases the water to hydrate conversion.
- Mixture of SDS + silver nanoparticles increases the initial apparent rate constant.
- Mixture of SDS + silver nanoparticles increases the CO_2 consumed within 120 min.

GRAPHICAL ABSTRACT



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ABSTRACT

The effects of synthetized silver nanoparticles and sodium dodecyl sulfate (SDS) on carbon dioxide hydrate formation rate and storage capacity have been studied in this work. Aqueous solution of SDS with concentrations of 300 and 500 ppm, suspension of silver nanoparticles with concentrations of 0.000045 and 0.00009 M, and the mixture of SDS (500 ppm) and silver nanoparticles (0.000045 M) were tested in a 460 cm^3 stirred batch reactor. The experiments were conducted at temperatures (273.65 and 275.65) K and initial cell pressures (2 and 3) MPa. Our results show that SDS and silver nanoparticles do not have significant effect on decreasing the induction time and increasing the storage capacity of CO_2 hydrates. However, the mixture of SDS and silver nanoparticles significantly increase the storage capacity of carbon dioxide. A diffusion-reaction kinetics model is used to predict the hydrate growth rate. Analyzing the growth rates at the start of hydrate formation show that, the addition of SDS and silver nanoparticles increases the apparent rate constant and the mixture of SDS and silver nanoparticles is most effective in enhancing the apparent rate constant.

1. Introduction

According to Kyoto protocol on climate change, many industrial countries committed to reduce the emission of some greenhouse gases. One of the main targets of this protocol is carbon dioxide. Therefore, CO_2 capture and sequestration is a very important area of research. There are different methods like absorption [1], adsorption [1], and membrane technology [2] for capturing the carbon dioxide from gas mixtures. These methods are generally expensive and finding cheaper technologies for separating carbon dioxide from gas mixtures seems to be necessary. Gas hydrate crystallization is one of the novel technologies for capturing carbon dioxide from flue and fuel gas mixtures [3–8]. Gas hydrates or clathrate hydrates are nonstoichiometric crystalline compounds consist of the small guest molecules trapped in a cage of water molecules networked together by hydrogen bonds [9,10].

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Nomenclature

A_i, B_i	Constants
C_i	Langmuir constant
f	Fugacity
M	Hydration number
N	Number of moles
P	Pressure
R	Universal gas constant
T	Temperature
V	Volume of the gas phase
υ	Molar volume
Z	Compressibility factor

Greek letters

θ	Fractional occupancy of cavities

Subscripts

0	Conditions of the cell at time $t = 0$
i	Counter
H	Hydrate
L	Large
RW_t	Water reacted
S	Small
S_0	The initial condition of the aqueous solution
STP	Standard conditions
t	Time t
H_t	The condition of hydrate produced
W	Water

Superscripts

L	Liquid
MT	Empty hydrate lattice

Gas hydrates have the potential for many industrial applications. However, slow formation rate of gas hydrates is one of the main problems of this process. Thus, investigating and promoting the kinetics of hydrate formation to benefit its positive applications (e.g. gas separation and storage) is very important. The promotion effect of some surfactants on induction time, growth rate, and storage capacity of gas hydrates has been well studied [11–21]. In 2013, Kumar and coworkers have investigated the influence of some additives on carbon dioxide clathrate hydrates [17]. Among their investigated surfactants, sodium dodecyl sulfate (SDS) was found to be most effective additive on increasing the hydrate formation rate, and storage capacity as well as reducing the induction time. Yang et al. investigated the effect of different concentrations of SDS on carbon dioxide hydrate formation and dissociation in porous media [22]. They found that 1000 ppm SDS presents the best effect on reducing the induction time [22]. The reported results by Lirio and coworkers in 2013 was different from the obtained results by Kumar et al., and Yang and coworkers [16]. Lirio et al., [16] reported that the effect of SDS on storage capacity of carbon dioxide is not significant. The literature results show that studying the kinetics of CO_2 hydrate formation in the presence of surfactants needs more attention.

Recently, some researchers have employed nanofluids to enhance the hydrate formation rate and storage capacity as well as reduce the induction time [23–26]. The thermal conductivity and the heat transfer of metal nanofluids suspensions are remarkably higher than conventional fluids [27–32]. Li and coworkers showed that the utilization of copper nanoparticles enhance the heat and mass transfer of the HFC134a hydrate formation process [24].

In the present work, the effect of SDS, synthetized silver nanoparticles, and the mixture of SDS/silver nanoparticles on induction time, storage capacity, and formation rate of carbon dioxide hydrate is investigated. A kinetic model is employed to predict the apparent rate constant of CO_2 hydrate formation and then the effect of tested additives on the initial apparent rate constants are compared. Finally, the effect of tested additives on "water to hydrate conversion" is discussed.

2. Experimental

2.1. Materials

Sodium dodecyl sulfate with purity of 98% and molecular formula $NaC_{12}H_{25}SO_4$ was purchased from Merck. Trisodium citrate dihydrate ($C_6H_5Na_3O_7{\cdot}2H_2O$), silver nitrate ($AgNO_3$), and hydrazine monohydrate ($N_2H_4{\cdot}H_2O$) were purchased from Merck, PanReac and Merck, respectively. Carbon dioxide with purity of 99.9% was supplied from Varian Gas. Distilled water was used in all experiments. Aqueous solutions were prepared using an accurate analytical balance with an uncertainty of ±0.1 mgr.

2.2. Apparatus

The schematic diagram of the experimental apparatus is shown in Fig. 1. The reactor is a jacketed stainless steel cell (with an effective volume of 460 cm^3). It has a valve for introducing and discharging aqueous solution and gas. For appropriate mixing of the gas and aqueous solution, an electromotor is used to rock the cell.

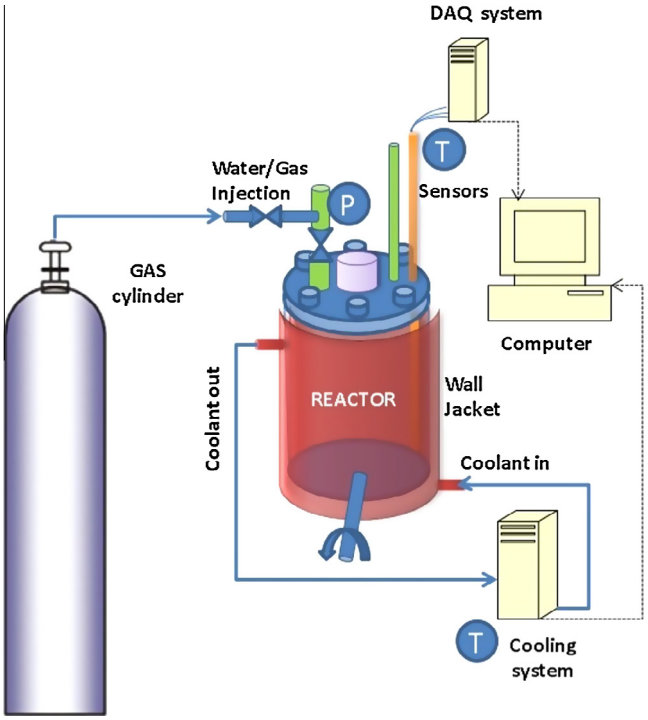

Fig. 1. Schematic illustration of the experimental apparatus.