



Influence of contact medium and surfactants on carbon dioxide clathrate hydrate kinetics

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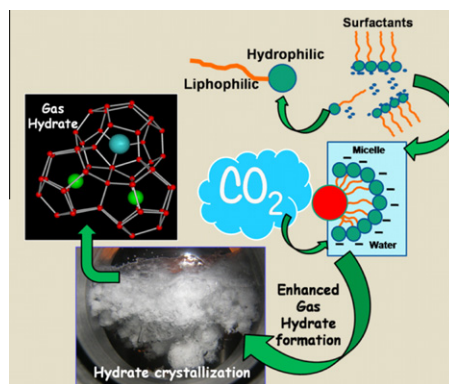
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HIGHLIGHTS

- ▶ Carbon dioxide (CO₂) hydrate formation kinetics in a fixed bed media.
- ▶ Major influence of surface area of silica gel on hydrate formation kinetics.
- ▶ Enhanced rate of hydrate formation in presence of surfactants.

GRAPHICAL ABSTRACT



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ABSTRACT

Carbon dioxide (CO₂) hydrate formation kinetic was investigated in a fixed bed crystallizer at constant pressure (3.55 MPa) and temperature (274 K). Porous media of three different silica gels were used, with a mesh size of 60–120, 100–200 and 230–400 having different surface area. The observed trends indicate that silica gel with larger surface area leads to higher gas consumption as well as reduces the induction time. The effect of pore diameter and particle size distribution has already been reported in a previous study [1]. In this study the effect of additives on hydrate formation kinetics were also investigated. The additives studied were nonionic surfactant Tween-80 (T-80), cationic dodecyltrimethylammonium chloride (DTACl) and anionic Sodium Dodecyl Sulphate (SDS). Out of the three surfactants used in this study, SDS was found to be most effective in enhancing the rate of hydrate formation as well as reducing the induction time. The current result shows significant improvement in water to hydrate conversion in silica gel media compared to quiescent water or surfactant–water system under similar conditions.

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1. Introduction

A number of methods can be used to capture carbon dioxide (CO₂) from its mixture; adsorption, absorption, and membrane separation are some of the conventional approaches, whereas gas hydrate based separation process or using metal organic frame-

works (MOFs) are novel approaches that are under investigation [2,3]. Capture of CO₂ by gas hydrate is one of the attractive technologies for reducing greenhouse effect [4–8]. Gas hydrates or Clathrates are compounds, in which the host molecule is water and the guest molecule is typically a gas or liquid [9,10]. There are number of reasons to study gas hydrates or clathrates, it is regarded as a potential source of natural gas [11–14], a potential unit operation for seawater desalination, gas fractionation, gas storage [15,16] and other novel applications like carbon dioxide capture, storage

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and sequestration [3–5,17]. Hydrate based crystallization process for CO₂ separation from its mixture has been studied extensively [5,6,18–20]. However a commercially viable hydrate based CO₂ separation process demands a rapid hydrate formation rate. Higher solubility of hydrate forming guest in water and larger contact area between the hydrate formers and water are very important. These two factors reduces the mass transfer resistance, resulting in faster hydrate formation rate [9,21,22]. Silica gel having a controlled pore structure and high surface area is extensively used in processes which require a powerful sorbing agent. In the present study porous media of silica gel in an unstirred vessel as crystallizer was employed to increase the contact area between hydrate formers [1,23,24]. Hydrate formation in silica gel pores also enhance the separation of CO₂ from a fuel gas mixture [25]. In addition small amount of surfactants were employed to enhance the solubility of hydrate forming guest in the water phase. Effect of pore size distribution of silica gel on hydrate formation rate has been studied in an earlier paper [1] and it was reported that larger pore size increases water to hydrate conversion. It was concluded that bigger pores will facilitate better diffusion of guest molecule in the porous media thus resulting in significant increase in water to hydrate conversion. Packed bed setup compared to stirred tank reactor is economical to operate (no stirring is involved) and it provides a large surface contact area between the gas and liquid. Gas hydrate formation in a stirred tank reactor is achieved through vigorous mixing, where continuously gas/liquid interphase is renewed between the guest (gas) and host (water) for hydrate formation. It has been reported in the literature that the performance of the stirred tank reactors for hydrate applications are limited by the mass transfer resistance at the gas/liquid interphase leading to low conversions of water to hydrates [21,26]. However, in a packed bed setup, porous material having large surface area to volume ratio will ensure the required contact between the guest and host for hydrate formation [21]. Effect of pore size distribution of silica gel has already been studied [1], and current work complements the previous work by studying the effect of surface area. Three different silica gels, type A (60–120 mesh), type B (100–200 mesh) and type C (230–400 mesh) were chosen for this study with almost similar pore diameter and different surface area with type C having the highest surface area and type A the lowest. (see the Supplementary data).

Hydrate formation in a non-stirred setup is quite slow, a thin film of hydrate forms on the water surface, and mass transfer across the film become rate controlling, resulting in slower kinetics and lower water to hydrate conversion. It has been reported that the obstructing hydrate film does not develop if a surfactant is added to the aqueous phase [27]. Surfactants [28,29] and certain water soluble polymers [30] have found to enhance water to hydrate conversion at certain concentration. Surfactant addition in presence of water allows the association of surfactant molecules in the form of micelles at concentrations above the critical micelle concentration (CMC). It has been proposed that micelles formation increases the solubility of hydrocarbon gas in the aqueous phase and also enhances hydrate growth by inducing the formation of hydrate crystals around the micelle in the bulk water phase [28,31]. But according to Watanabe et al. [32], the critical factor affecting the hydrate forming behavior is the solubility, instead of the CMC, above which SDS forms a hydrated solid in the aqueous phase. Di Profio et al. [33] reported that there was no micelle formation over the SDS concentration ranging from 230 ppm to 2000 ppm and CMC could not be detected before the concentration was increased to ~2300 ppm. It has been reported in the literature that the capillarity driven supply of the water into the porous hydrate layers is responsible for enhancement in the hydrate formation in presence of a surfactant [34–36]. Sodium Dodecyl Sulphate (SDS) is clearly the surfactant of choice for most of the research on

gas hydrate applications [32,35,37–40]. SDS is an anionic surfactant and it has been reported that an anionic surfactant fares better in improving the water to hydrate conversion rate compared to cationic and nonionic surfactants [28,30,41]. It can be said that utility of surfactants as a promoter for hydrate crystallization has been clearly established. However, the qualitative knowledge obtained so far is system specific. Dependencies on the surfactant concentration for hydrate-formation rate and the final water to hydrate conversion ratio has been established for many guest species. However, such dependencies may vary more or less with the species of the guest gas and the surfactant used. Compared to methane, carbon dioxide is slightly polar and much more soluble in liquid water; it would be interesting to see if the effect of different surfactant and its concentration is equally significant in terms of rate of hydrate growth, and water to hydrate conversions. This study will help in developing a suitable surfactant aided commercial processes for carbon dioxide separation from flue and fuel gases. In this work, we have studied all the three type of surfactants at varying concentration to study its effect on water to hydrate conversion. SDS serves the purpose for anionic surfactant, Tween-80 a nonionic surfactant and dodecyltrimethylammonium chloride (DTACl) a cationic surfactant [33,42]. This work will complement our previous work [1] and will be helpful to those working on gas hydrate based CO₂ separation studies.

2. Experimental

2.1. Materials

Carbon dioxide gas with a certified purity of more than 99% was supplied by De-luxe Industrial Gases, India. Silica gels with $\geq 99\%$ purity of LR grade was purchased from Rankem Ltd. Surfactants, Tween-80 (LR Grade), dodecyl trimethyl ammonium chloride (LR Grade) and SDS (SQ Grade) with minimum 98% purity were purchased from Rankem Ltd., SRL Pvt. Ltd. and Fisher Scientific Ltd. respectively. All the materials were used without further purification.

2.2. Apparatus

The apparatus is shown in Fig. 1. It consists of a 500 cm³ SS-316 high-pressure hydrate crystallizer (CR) equipped with an internal cooling coil. The top cover plate of the crystallizer had six ports each equipped with a Swagelok connector. These ports were used for inserting three thermocouples, supplying gas (inlet), vent and pressure transducer. Three thermocouples with ± 0.1 K accuracy are used to measure the temperature; T-1, T-2 and T-3. All pressure measurements are made with pressure transducers, with a range of 0–100 bar and accuracy of 0.075% of the span. The crystallizer is immersed in a water bath containing a 50/50 wt% methanol/water mixture. Both the crystallizer cooling coil as well as the water bath is connected to a chiller (Julabo-FS18), which maintains the temperature in the hydrate crystallizer and the supply vessel (SV) constant. A stirrer is used inside the water bath to uniformly distribute the cooling liquid in the water bath. As we know hydrate formation predominantly depends on the degree of super-cooling, more hydrate forms near the crystallizer wall than that at the center of the crystallizer (due to heat transfer limitation). To avoid this problem, a cooling coil is provided in the fixed bed portion of the crystallizer for additional cooling. The gas-supply line connecting a high-pressure gas cylinder to the crystallizer was equipped with a pressure regulator, a mass flow controller (MFC) (Brooks model F10974-001, with a Flow rate 0–5 ml/min at operating pressure) and a digital pressure gauge (PPI model). This allowed us to measure the instantaneous rate of gas supply into the crystallizer and

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