

Investigating the effects of hydrophobic and hydrophilic multi-wall carbon nanotubes on methane hydrate growth kinetics

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HIGHLIGHTS

- The hydrophobic MWNTs' growth enhancement plateaus at higher loadings.
- At low loadings, the hydrophilic MWNTs' effects behave non-linearly with loading.
- At higher loadings, the hydrophilic MWNTs' enhancement increases with loading.

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ABSTRACT

Currently, gas hydrates have sparked the interest of many industries for their potential use in natural gas transportation, component separation and carbon dioxide sequestration. In order to optimize the efficiencies of such applications, there has been a pronounced focus on finding techniques and additives that promote hydrate growth. Previous studies have found that the addition of multi-wall carbon nanotubes (MWNTs) to methane hydrate systems greatly enhances production. In this study, the growth rates of methane hydrates were measured in the presence of as-produced (hydrophobic) and plasma functionalized (hydrophilic) MWNTs. For each condition, the effect of MWNT loading in the aqueous phase was determined. At higher concentrations, the hydrophobic MWNTs produced an enhanced growth rate whose effect plateaued with MWNT loading. The hydrophilic MWNTs' effect had an initial local maximum at lower concentrations and then followed to increase almost linearly with an increase in concentration.

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1. Introduction

Clathrate hydrates are non-stoichiometric crystalline structures composed of inclusion molecules bound in a water lattice. Discovered in 1810 by Sir Humphry Davy, their initial research motivation was purely academic (Davy, 1811). In the 1930s, an industrial relevance surfaced when it was found that hydrates were blocking oil and gas pipelines (Hammerschmidt, 1934). Current research activities aim at the generation of these compounds for such uses as the transportation and storage of natural gases, carbon dioxide sequestration and in novel separation techniques (Sloan and Koh, 2008; Gudmundsson and Borrehaug, 1996; Harrison et al., 1995; Linga et al., 2007; Sun et al., 2007).

In order to employ hydrate structures for their potential use in the aforementioned technologies, it is of great interest to study compounds and/or structures that can aid in their formation. One

such promoter are multi-wall carbon nanotubes (MWNTs), which have been found to increase methane hydrate yields (Park et al., 2010, 2012; Kim et al., 2011). The issue with adding such nanoparticles to an aqueous system is that the MWNTs are naturally hydrophobic, which causes them to agglomerate and settle out of solution (Park et al., 2012). To enhance their stability, the MWNTs are often mixed in with surfactants or are chemically treated (Vandsburger et al., 2009). Current advances have now allowed MWNTs to be stabilized by functionalizing their surface with oxygen containing groups via plasma treatment (Vandsburger et al., 2009). This allows the MWNTs to remain dispersed in an aqueous solution for extended periods of time (> 2 years demonstrated thus far) through the addition of covalently bonded oxygenated functionalities such as carboxyl, carbonyl, and hydroxyl groups (Hordy et al., 2013).

The hydrate formation process can be separated into three distinct steps, namely saturation, induction and growth (Sloan and Koh, 2008). A schematic of the process in terms of hydrate former consumption versus time can be found in Fig. 1. In order to initiate hydrate formation, the inclusion molecules must first dissolve into

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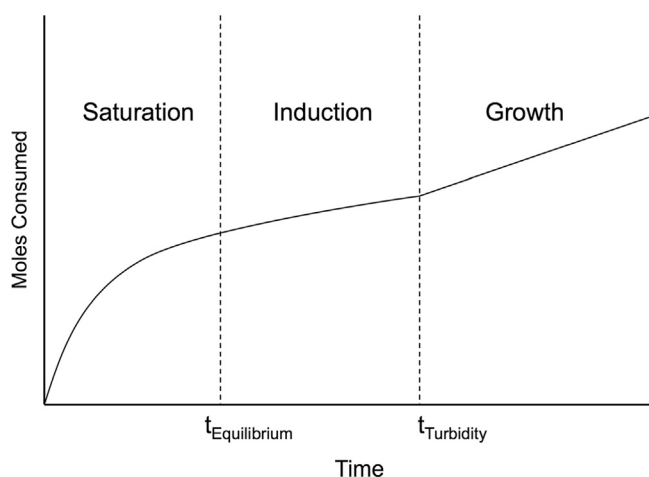


Fig. 1. Schematic of a gas hydrate former consumption curve.

an aqueous solution. At a point of time, the solution will become saturated, denoted as $t_{\text{Equilibrium}}$. After this, the solution will become supersaturated as more molecules continue to dissolve. Hydrates can only form when a solution enters the supersaturated regime (Sloan and Koh, 2008). In this step, often called the induction period, small clusters of hydrate nuclei continually form and dissociate until a critical cluster radius is achieved, whereby the nucleus has reached energetic stability (Sloan and Koh, 2008). For the methane hydrate, it is estimated that this critical nucleus size ranges from 30–170 Å (Englezos et al., 1987). The formation of this nucleus is marked as $t_{\text{Turbidity}}$ and designates the onset of autocatalytic hydrate growth. In this third growth step, the initial consumption of the inclusion bodies increases linearly with time. It is this linear portion that is of interest for the analysis of growth kinetics.

This current study aims to investigate methane hydrate growth rates in the presence of both as-produced (hydrophobic) MWNTs and plasma functionalized (hydrophilic) MWNTs at various concentrations. While previous studies have measured the total uptake of the hydrate forming gases at the end of multiple hours of growth, none have examined the kinetic growth rates as a function of MWNT loading (Park et al., 2010, 2012; Kim et al., 2011). Furthermore, the concept of utilizing plasma functionalized MWNTs in gas hydrate systems is completely novel.

2. Materials and methods

A schematic of the experimental apparatus can be seen in Fig. 2. The experiments were carried out in a custom-built stainless steel 316 crystallizer. Its design specifications allow the unit to withstand pressures of up to 20 MPa. The internal diameter of the crystallizer is 7.62 cm and its walls are 4.45 cm in thickness. The capacity of the chamber is 610 mL. It contains two polycarbonate windows that allow for visual observation of the hydrate system. The liquid solutions are injected through a 0.32 cm NPT sample port. The temperatures of both the liquid and gas phases are monitored with general-purpose platinum RTDs (Omega, with a Class A accuracy of $\pm 0.154^\circ\text{C}$ at the experimental conditions). The pressure in the crystallizer is monitored with a Rosemount 3051 Smart Pressure Transmitter. These transducers have an operating range of 0–13,780 kPa and an accuracy of 0.04% of the span. In order to avoid mass transfer limitations, a 5.08 cm long magnetic stir bar was introduced at the base of the crystallizer. It was spun with a 1/8 HP, 90 V DC, 1750 RPM Leeson Electric Motor which was attached to a Neodymium External Horseshoe

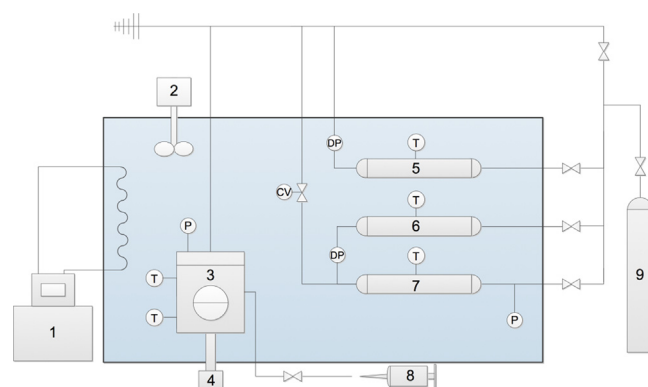


Fig. 2. Simplified schematic of the experimental set-up. 1—Chiller, 2—Electric stirrer, 3—Crystallizer, 4—Magnetic stirrer, 5—Reactor bias, 6—Reservoir bias, 7—Reservoir, 8—Sample injection, 9—Methane cylinder. T, P, and DP represent temperature, absolute pressure, and differential pressure respectively, while CV represents the control valve.

magnet. Throughout hydrate formation, the motor speed was set at 525 RPM.

In order to control the temperature of the system, the crystallizer was submerged in a bath with a 50/50 volume mixture of water and ethylene glycol. The temperature of this bath is controlled by a Neslab RTE 740 chiller. The chiller also uses a 50/50 volume mixture of water and ethylene glycol as its cooling fluid, which can operate at a range of -40 to 200°C . The accuracy on the temperature measurement is 0.01°C . To maintain homogeneous thermal conditions inside the bath, a Leeson Direct Current Permanent Magnet Motor was employed to mix the bath fluid.

A gas reservoir tank was used to maintain isobaric conditions in the crystallizer throughout each experiment. The reservoir supplied gas via a Baumann 51000 Low Flow control valve. This chamber is also placed inside the cooling bath and its temperature was measured with the same type of RTD found in the crystallizer. The absolute reservoir pressure is also monitored with the same model pressure transducer used in the crystallizer. Bias chambers for both the reservoir and the crystallizers were also submerged with their respective temperatures measured via RTDs. Differential pressure readings between the reactor and its bias as well as the reservoir and its respective bias are monitored via a Rosemount 3051 Smart Pressure Transducers with an operating range of 0–2000 kPa and an accuracy of 0.04% of the span. The reactor differential pressure is used to instruct the control valve's operation while the reservoir differential pressure is used to accurately measure gas consumption.

The methane used in the experiments is purchased from MEGS and is of Ultra High Purity. The water used was treated via reverse osmosis ($0.22\ \mu\text{m}$ filter, conductivity of $10\ \mu\text{S}$, total organic content of $< 10\ \text{ppb}$). The MWNTs were produced by thermal chemical vapor deposition using acetylene as the carbon source and stainless steel (SS) meshes as the growth surface. Both hydrophobic and hydrophilic MWNTs have approximate diameters of 31.4 nm and lengths of $1\ \mu\text{m}$. The hydrophilic MWNTs were plasma functionalized using a capacitively-coupled RF glow discharge in a $\text{Ar}/\text{C}_2\text{H}_6/\text{O}_2$ mixture to add covalently-bound oxygen functionalities (Hordy et al., 2013). X-ray photoelectron spectroscopy (XPS) studies of the MWNTs show that oxygen comprises approximately 21% of the atomic composition of their surfaces (Hordy et al., 2013). Analysis of the surface of the MWNTs revealed the presence of hydroxyl (COH), carbonyl (C=O), and carboxyl (COOH) groups (Hordy et al., 2013). Contact angle (CA) measurements of the as-produced MWNTs on the SS substrate are hydrophobic, with a static CA of 103.4° , while the functionalized MWNTs are superhydrophilic with

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