



# Kinetics of carbon dioxide gas hydrates with tetrabutylammonium bromide and functionalized multi-walled carbon nanotubes



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## ABSTRACT

The effects of oxygen-functionalized multi-walled carbon nanotubes (MWCNTs) on tetrabutylammonium bromide (TBAB)-water-carbon dioxide semi-clathrate system was investigated. A system comprised of 9.5 ppmw MWCNTs and 40 wt % TBAB was chosen and the average gas consumption rate was calculated for different conditions. At 14 °C, the average gas consumption rate during growth decreased to a plateau with increasing induction time at 3.0 °C subcooling for systems with and without MWCNTs. The addition of MWCNTs increased the gas consumption rate during growth for induction times less than one hour but did not affect it at longer induction times. The maximum gas consumption enhancement from the added MWCNTs was 15%. Dissolution runs at equilibrium conditions indicated that the presence of MWCNTs improved the dissolution rate of carbon dioxide gas into the liquid by lowering the time constant  $\tau$  by 5%. This suggests that the gas-liquid interfacial resistance of carbon dioxide gas mass transfer is not the limiting factor for hydrate growth in this TBAB semi-clathrate system with and without nanoparticles. At a lower subcooling of 1.5 °C, there was no significant difference in the gas consumption rates with the addition of MWCNTs, due to prolonged induction times.

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## 1. Introduction

Global warming and climate change have become major topics of worldwide concern. Due to its high stability and concentration in the atmosphere, carbon dioxide gas is the largest contributor to the greenhouse effect. Reducing carbon dioxide emissions is an international priority as nations strive to meet the increasingly stringent commitments made at forums such as the 2015 United Nations Climate Change Conference in Paris [1]. A multifaceted approach is needed to achieve this, and developing effective carbon dioxide removal methods is a viable solution. According to the U.S. Department of Energy, novel gas hydrate technologies are promising methods for capturing and storing carbon dioxide gas [2]. Carbon dioxide recovery from flue gas using gas hydrate technology has been shown to be thermodynamically possible [3–6]. Gas hydrates are nonstoichiometric crystalline compounds that arise when a gas or volatile liquid is encapsulated inside cavities formed

by water molecules. The guest molecule must be of correct size to fit inside and stabilize the crystal lattice via weak van der Waals forces with the host water molecules [7]. There are over 180 different molecules that form gas hydrates; the most relevant for research and industrial applications being methane, ethane and carbon dioxide [8]. Transportation and storage of natural gas, methane or carbon dioxide have been discussed as feasible alternatives to current technologies because gas hydrates have high gas storage capacities. One single cubic meter of methane hydrate can release up to 160 cubic meters of methane gas [9]. In addition, separation of gases using gas hydrate technologies has been extensively discussed in literature and offers a promising opportunity for carbon dioxide capture [10–13]. The lack of scalability studies as well as slow and unpredictable hydrate formation kinetics have prevented large scale development of the proposed technologies [14].

One limitation of a hydrate-based technology is the high pressure and low temperature conditions needed for hydrate formation. This can be addressed using thermodynamic promoters that shift the gas hydrate equilibrium to more energetically favourable conditions. One category of thermodynamic promoter chemicals is called semi-clathrates since the molecule incorporates itself inside the water lattice, consequently stabilizing

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the structure and significantly lowering the hydrate energetics. These semi-clathrate forming compounds are typically ionic molecules that have their cationic part occupying cages like guests and their anionic part involved in the cage formation alongside water. The tetrabutylammonium bromide (TBAB) salt is the most commonly used semi-clathrate forming promoter. At atmospheric pressure, TBAB hydrates can form at temperatures up to 12.4 °C [15]. Previous studies have generally focused on the thermodynamics of TBAB hydrates, namely the equilibrium temperature, pressure and TBAB liquid concentration with single and multiple guest gases [16–19]. Multiple groups have demonstrated the possibility of separating carbon dioxide from flue gases using TBAB hydrates [20,21]. Li et al. showed that TBAB shortens induction time and accelerates hydrate kinetic formation rates [20]. In another report, it was shown that a 40–45 wt % TBAB solution may be a promising cold storage material for air conditioning systems due to its high phase change temperature and its improved hydrate conversion [22]. Recently, the kinetic behaviour of TBAB and carbon dioxide gas hydrates was thoroughly investigated at temperatures ranging from 13.85 °C to 15.85 °C [23]. Other semi-clathrate forming salts, such as tetrabutylammonium nitrate (TBANO<sub>3</sub>) and tetrabutylammonium fluoride (TBAF) have also been studied and proven feasible for use in hydrate based gas separation applications [24–26].

Carbon nanotubes (CNTs) show great potential for a wide range of products and applications, including the use as kinetic promoters in the field of gas hydrates. CNTs are self-assembling rolled sheets of graphene that exhibit excellent mechanical strength in addition to high thermal and electrical conductivity [27]. Many different synthesis strategies and applications exist to produce various types of carbon nanostructured materials [28–31]. Carbon nanotubes have a very high aspect ratio, which makes them attractive for use as a kinetic gas hydrate promoter [32]. The nanotubes are dispersed in a base fluid to create a “nanofluid” that can be used as the hydrate-forming liquid phase [33]. Oxygen-functionalized multi-walled carbon nanotubes (MWCNTs)-hydrate experiments were first reported in 2010 by Park et al. [34]. They used 40 ppmw MWCNT in water and observed an increase in methane consumption and hydrate growth rate [34,35]. Pasiaka et al. reported a slight hydrate growth enhancement and increased dissolution rates using 1 to 10 ppmw MWCNT [36,37]. Additionally, many groups reported a significant decrease in induction time with the presence of nanoparticles [38–40]. At this point, few publications have investigated the effect of combining a thermodynamic promoter such as TBAB with a kinetic promoter such as MWCNT. The addition of 200–500 ppmw silver nanoparticles, 0.1 wt % SDS and 0.5 to 1.0 wt % cyclodextrin to a gas hydrate system resulted in an increase in carbon dioxide gas consumption and apparent kinetic growth rate constant [41]. Furthermore, the combination of 10–60 ppmw MWCNTs with 19.1 wt % tetrahydrofuran also improved the kinetic growth rate [42]. In a system with 20.3 wt % tetrahydrofuran (THF) at atmospheric conditions, it was shown that the addition of MWCNTs decreased the subcooling required for nucleation and enhanced the system’s ability to expel the heat of formation via an increase in effective thermal conductivity [43].

The goal of this paper is to observe the effect that the addition of MWCNTs has on the hydrate growth rate and dissolution rate (at three-phase equilibrium conditions) in a TBAB-water-carbon dioxide hydrate system. To the best knowledge of the authors, this is the first time that a report discusses the combination of TBAB and MWCNTs in any gas hydrate system. Semi-clathrate kinetic and dissolution analysis with the addition of nanoparticles is novel and provides crucial information for the possible hydrate based applications using these compounds.

## 2. Materials and methods

### 2.1. Experimental setup

A simplified diagram of the experimental setup can be found in Fig. 1. A detailed description of the experimental setup and procedure can be found in a previous report [44]. A 612 mL stainless steel reactor is submerged in a temperature-controlled 20% by volume ethylene glycol-water bath. The inner reactor has dimensions of 4.5 inches height and 3.25 inches diameter. The reactor and temperature-controlled bath are equipped with a MM-D06 magnetic stirrer from Pressure Product Industries with a standard magnetic stir bar with spinning ring from Cole Parmer. The stirrer speed was fixed at 560 rpm. A reservoir gas tank is employed to keep the reactor pressure constant during experiments with a Baumann 51000 control valve. The valve is controlled by the difference in pressure signals between the reactor bias gas tank and the reactor. Pressures are monitored using Rosemount pressure transducers configured to a span of 0–14,000 kPa for absolute pressure measurements and 0–2000 kPa for differential pressure measurements, with an accuracy of 0.065% of the given span. Resistance temperature detectors (RTD) probes from Omega record temperatures from the reactor liquid, reactor gas and reservoir tank. The reactor liquid RTD being located near the bottom of the reactor is always well below the liquid line, while the reactor gas RTD being located near the top of the reactor is always well above the liquid level line. Carbon dioxide gas with a purity of 99.995% was obtained in Canada from MEGS Inc. The water was treated in-house by reverse-osmosis with a 0.22 μm filter and it has a conductivity of 10 μS and total organic content less than 10 ppmw. 50 wt % TBAB in liquid water was obtained from Sigma Aldrich United States and used to prepare the 40 wt % TBAB mixture used in this study. The solution of 40 wt % TBAB was selected because this value is near the stoichiometric amount of TBAB required to form hydrates and the thermodynamic equilibrium data was available at this concentration making it possible to fix the driving force [19].

Oxygen functionalized multi-walled carbon nanotubes were produced following the procedure developed by Hordy et al. [27]. A 316 stainless steel mesh acts as a support material and catalyst for MWCNT growth. The stainless steel mesh was placed on a ceramic boat, itself inserted into a quartz tube furnace for MWCNT growth by thermal chemical vapor deposition. The carbon source, acetylene, was flowed for 4 min at a furnace temperature of 700 °C, conditions that led to the growth of a dense MWCNT forest on the mesh. The as-produced MWCNT-covered mesh was then exposed to a capacitively-coupled radio-frequency (13.56 MHz) glow discharge plasma in an Ar/O<sub>2</sub>/C<sub>2</sub>H<sub>6</sub> gas mixture (250/5/1 sccm). Exposure to the plasma led to the addition of oxygen-containing

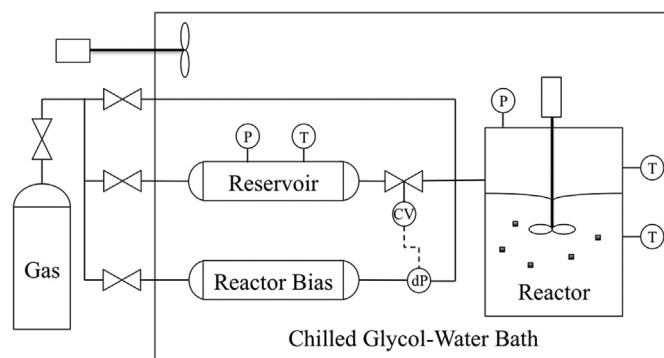


Fig. 1. Schematic of the experimental setup.

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