

Effect of Additives on Hydrate Growth

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1. Introduction

Gas hydrates are preferentially formed over hexagonal ice during water's liquid-to-solid phase change in the presence of a gas molecule dissolved in the water. As the phase change begins, water molecules self-organize into a crystal lattice via hydrogen bonds, creating cage structures that can trap gas molecules found in solution ^[1]. The presence of the gas molecule in the cage stabilizes the lattice energy by dispersing van der Waals forces ^{[2][3]}. The gas hydrate crystallizes out of the bulk water system forming a particle mass, which continuously grows while conditions favor hydrate formation and gas molecules are available. First formally described in 1811 by Sir Humphrey Davy ^[4], increased research motivation came from the occurrence of gas hydrates in oil and gas industry applications identified in the early-mid 20th century ^[5]. Much of the research that followed focused on the prevention of gas hydrate formation and gave rise to the flow assurance engineering discipline ^[2].

Recently, several process technologies involving the formation of gas hydrates have been proposed. They take advantage of the physical properties of gas hydrates to help accomplish a process. The high gas-to-liquid volume ratio and the gas selectivity that occurs as gas species are trapped in hydrate cages are two important properties leveraged by the proposed technologies. These include pre- and post-combustion carbon capture from flue gas ^{[6][7][8][9]}, gas storage and separations ^{[10][11][12][13][14][15]}, water desalination ^[16] and treatment ^[17], or even fruit juice concentration ^[18]. These new research interests have motivated the study of new gas hydrate promoter additives such as carbon nanofluids ^{[19][20]}. Additionally, many of the new process technologies mentioned above involve batch and semi-batch flow systems that are found in (and near) gas hydrate formation conditions. These technologies would benefit from the rheological characterization of gas hydrate systems in the pre-nucleation stage and during hydrate formation. System viscosity information is critical in the design and control of such processes. To this end, rheological phase diagrams of methane and carbon dioxide gas hydrates in pure water have been recently developed ^[21].

The thermal, mechanical, and interfacial properties of gas hydrates are crucial in expanding the description of gas hydrate formation, as they help describe the structure's interaction with the environment. These properties of hydrates have been studied for sl and sII hydrates primarily, with sH hydrate studies more recently ^{[22][23][24][25][26][27]}. For example, the mechanical properties are critical to determining the strength and flexibility of the structure, and critically understanding the effect of guests on these can determine how suitable the structure is to the desired application ^{[24][28][29]}. For example, the Young's modulus, which is used to describe a structure's resistance to deformation, was found to be highest for nitrogen-neohexane sH hydrates ^[30], helping guide further work into the strongest structure. Interfacial properties have also been studied recently to help clarify what exactly is happening at the atomic scale during gas hydrate formation ^{[27][31][32][33][34]}. By developing correlations for the surface tension as functions of temperature, physical changes in gas hydrate systems can be predicted prior to an application's implementation, providing a foundation to the critical applications ^{[27][35]}. Other literature has also examined the use of certain surfaces to manipulate the nucleation interface for desired behavior ^{[36][37]}.

Gas hydrate inhibitor research has previously focused on thermodynamic inhibitors such as ethylene glycol or methanol. However, thermodynamic inhibitors require high volumetric fractions in solution for effective inhibition. This imposes economic and operational constraints as large volumes of inhibitors lower the volumetric transport capacity of process streams and incur high operational costs ^[2]. Recent work on gas hydrates inhibitors has focused on kinetic hydrate inhibitors (KHIs) as they are effective at lower concentrations (below 1 wt.%) compared to thermodynamics inhibitors ^[38]. Promising candidates for kinetic hydrate inhibition tend to have the ability to adsorb to the surface of polar hydrate crystal

surfaces while also being soluble in water ^{[39][40]}. This can be achieved by the activity of hydrophobic and hydrophilic groups, respectively, which makes amphiphilic block copolymers an attractive choice for kinetic hydrate inhibition ^{[41][42]}. Some other breakthrough studies on promotion and inhibition include work on the effect of a magnetic field ^{[43][44]} on formation, the use of anti-agglomerants ^[45], the mixed effects of metal nanoparticles on methane hydrate formation ^[46], and the impact of wax molecules on methane hydrate formation ^{[47][48][49][50][51]}.

The rheological characterization of gas hydrates requires the use of highly specialized and costly experimental equipment ^{[52][53][54][55][56]}. This restricts the ability of such research to be conducted. Additionally, researcher group has reported experimental limitations (kinetic, diffusion, and heat effect) to high-pressure rheology experiments of pure water gas hydrates ^[21]. Recent work on the inhibitory and promotional activities of gas hydrates has pointed toward molecular scale phenomena, which can be difficult to describe through experimental methods alone fully ^{[19][41]}. A variety of computational research methods can be utilized to solve such problems, including density functional theory (DFT) and molecular dynamics (MD).

2. Effects of Additives on Hydrate Growth

2.1. Multi-Walled Carbon Nanotubes

Multi-walled carbon nanotubes are hydrophobic as produced. Once either oxygen or amine becomes functionalized through a plasma process, as described above and detailed in Hordy et al. ^[57] and Legrand et al. ^[58], the material becomes hydrophilic. The hydrophilicity affects the material's ability to form hydrogen bonds in water. The effect of as-produced hydrophobic MWCNT and functionalized hydrophilic MWCNT on the growth kinetics of methane and carbon dioxide gas hydrates were explored. Oxygen functionalized MWCNT was used to examine their effects on methane systems, while amine functionalized MWCNT was used for carbon dioxide systems. The groups found on the surface of MWCNT after amine functionalization can form temporary bonds with carbon dioxide ^{[59][60][61]}. This makes this type of functionalization relevant to carbon dioxide gas hydrates systems.

The crystallizer system described above was used to measure system pressures and temperatures to study the growth kinetics of MWCNT-loaded systems. In the case of methane hydrates systems, both the hydrophobic and hydrophilic (oxygen functionalized) MWCNTs enhanced the growth rates of methane hydrates compared to pure water baselines. Hydrophobic MWCNT enhanced growth rates by approximately 6% (5 and 10 ppm MWCNT), while hydrophilic MWCNT enhanced growth rates by as high as 16.3% (0.1 and 10 ppm MWCNT) ^[62]. Previous research has observed the increase in gas mass uptake into aqueous solutions containing nanoparticles ^{[63][64][65]}, and that the interfacial area between liquid and gas phases increases in the presence of nanoparticles ^[65]. This work pointed toward this same effect for the case of MWCNT. The loading of nanoparticles in the system was also observed to affect the growth rate enhancement of hydrates. Concentrations above 1 ppm of hydrophobic MWCNT were found to have enhancement effects, while hydrophilic MWCNT was observed to have two regions of enhancement. At 0.1 ppm, the system experienced maximal enhancement, followed by a decrease at 0.5 and 1 ppm. Finally, the growth rate enhancement continued linearly between 5 and 10 ppm ^[66]. The two regions of enhancement were attributed to diffusivity enhancement from micro-scale liquid volume displacement from Brownian motion at low loading followed by free mean path limitations overcoming this diffusivity enhancement at high loading ^[62].

Identical experimental studies were performed to investigate the effects of amine-functionalized MWCNT in carbon dioxide hydrate systems. Both as-produced hydrophobic MWCNT and hydrophilic amine functionalized MWCNT were found to enhance carbon dioxide hydrate growth at lower concentrations, which was attributed to enhanced mass transfer effects ^[66]. However, for similar loading concentrations, the hydrophilic functionalized MWCNT was observed to enhance hydrate growth to a greater extent than as-produced MWCNT due to its greater affinity to carbon dioxide molecules ^[66]. Decreases in growth rate enhancements at higher loading concentrations were attributed to heat effect limitations from the nucleation of larger amounts of hydrates. The temperature increase from the exothermic crystallization reaction was found to be high enough to self-limit further hydrate formation. Additionally, it was found that the presence of amine-functionalized MWCNT did not have any considerable effect on the solubility or rate of dissolution of carbon dioxide in water ^[66]. Generally, the results from hydrophobic and hydrophilic MWCNT studies have pointed towards mass transfer enhancements arising from molecular scale phenomena of nanoparticles on the systems, which can be overcome by increased nanoparticle loading. Insight into the fundamental phenomena involved in these observations may be achieved from computational methods such as molecular dynamics.

2.2. Graphene Nanoflakes

The crystallizer experimental setup described above was also used to investigate the effect of as-produced (hydrophobic) and oxygen functionalized (hydrophilic) graphene nanoflakes (O-GNF) on the growth rates of methane gas hydrates. Similar to the results for the MWCNT studies described above, both hydrophobic and hydrophilic forms of GNF enhanced the methane hydrate growth rates measured compared to measurements performed in pure water baselines [19]. However, the enhancements were much larger than those observed in the presence of MWCNT. Enhancements as great as 101% for as-produced hydrophobic GNF (1 ppm GNF), and as high as 288% for hydrophilic oxygen functionalized GNF (5 ppm O-GNF) were estimated [19]. Both maximums in growth rate enhancements measured were followed by decreased enhancements at higher loading. Nanoparticle loading effects on hydrate growth rate enhancements were attributed to small and large-scale agglomeration effects combined with mean free path limitations. It was reported that hydrophobic as-produced GNF could experience agglomeration at lower loading concentrations in solution and thus result in limited enhancements to hydrate growth [19]. As loading increases, agglomeration is overcome by the increased liquid–gas interfacial area available for mass transfer, which causes gains in the hydrate growth enhancement achieved. However, at the highest loading, large-scale agglomeration becomes the dominant effect resulting in a reduction in the enhancement effect. The use of hydrophilic O-GNF in solution was observed to dramatically increase hydrate growth rates up to 288% in a linear fashion [19]. In the case of hydrophilic O-GNF, agglomeration did not play a big role in the effects observed. Instead, the enhancement was attributed to increased diffusivity and mass transfer at lower concentrations. These effects were negated by reduced free mean paths at mid-range loading concentrations (5 ppm) [19]. Finally, at the highest loading concentration (10 ppm), the free mean path limitations were described to be overcome by the increased O-GNF surface area available to methane.

The results reported for graphene nanoflakes point to similar load effects on hydrate growth rates as the ones described for MWCNT. Hydrophobic and hydrophilic GNF and MWCNT were described to interact differently between themselves and with the system, creating limitations to gas hydrate growth rate. For both types of nanoparticles, the enhancements observed fell under different regions of nanoparticle load effect leading to an overall non-monotonic load effect. Different molecular scale phenomena were used to explain the non-monotonic behavior. Agglomeration, diffusivity, free mean path, and nanoparticle surface area were provided as possible contributors to the detected effect. Most, if not all, of these may be further examined computationally. Due to their scale, molecular dynamics is a promising methodology for further examination of these recently characterized effects.

2.3. Polymer Inhibitors

The initial consideration of kinetic hydrate inhibitors (KHIs) involved commercially available poly(vinylpyrrolidone) (PVP). The efficacy of hydrophobic PVP as a gas hydrate inhibitor was quantified by its effect on methane hydrate growth rate and on the concentration of methane in the liquid phase [67][68]. PVP with different molecular weights were used—10,000 g/mol (PVP10), 40,000 g/mol (PVP40), and 360,000 g/mol (PVP360)—over a range of loading concentrations (0.07 to 20,000 ppmw). PVP was shown to lose inhibitory capacity with increased reactor pressure (increased hydrate pressure driving force) and various molecular weights (polymer chain lengths) were shown to have little impact on the inhibitory activity at a given loading concentration [67]. It was determined that PVP had a negligible effect on methane solubility in water and a significant effect on the supersaturation of methane during hydrate growth [67][68]. The higher liquid concentration was attributed to a reduction in surface area available for hydrate growth due to the uptake of methane by PVP as it adsorbs to the hydrate crystal surface [68].

Amphiphilic molecules have both hydrophilic and hydrophobic subunits or groups and can act as surfactants in solvating a hydrophobic species or material in a hydrophilic solvent. The use of amphiphilic block copolymers as KHIs were explored in various forms. Three types of block copolymers were studied (1) poly(vinyl alcohol) (PVA), (2) poly(vinylpyrrolidone) (PVP), and (3) poly(vinyl caprolactam) (PVCap) hydrophilic base units [41][42]. These base units were combined using a switchable RAFT chain transfer agent (CTA) to attach relatively short poly(styrene) (PS) or poly(pentafluorostyrene) (PPFS) hydrophobic segments. The reduction in methane consumption during the hydrate growth phase was measured for systems inhibited by each block copolymer and compared to base inhibition by commercially available homopolymers PVP and PVA. Details on the experimental setup and procedures are found elsewhere [41][42]. The key results are summarized in **Table 1**, where columns contain hydrophilic segments while rows contain hydrophobic segments of the copolymer. Values in **Table 1** correspond to the block copolymer combination between the segments (e.g., 49% for PVA-PS and 76% for PVP-PPFS). Additionally, **Table 1** contains the reduction of methane consumption for hydrophilic PVA, PVP, and PVCap KHIs on the first row.

Table 1. Reduction in methane gas mole consumption during hydrate growth phase for hydrophilic polymers PVA, PVP, and PVCap, and amphiphilic block copolymer combinations of PVA, PVP, PVCap with PS and PPFS [41][42].

PVA	PVP	PVCap	
	%	%	%
-	27	51	53
PS	49	59	56
PPFS	63.5	76	73

Amphiphilic molecules tend to agglomerate and form micelles when above their critical micelle concentration (CMC) [69]. For instance, in a hydrophilic solvent, the hydrophobic groups in amphiphilic molecules agglomerate to form micelles when above their CMC; likewise, the hydrophilic groups can initiate micelle formation in a hydrophobic solvent. The formation of micelles can obstruct or limit the surfactant activity of amphiphilic molecules and thus reducing their inhibitory capabilities in the context of gas hydrate growth. As such, the CMC is an important characteristic of amphiphilic block copolymers and they were determined for the various block copolymers examined by Rajput et al. [41][42]. There are several methods adequate for measuring the CMC of polymer solutions, including density and viscosity, light scattering, and surface potentials [70][71][72][73]. In the work by Rajput et al. [41][42], the zeta surface potential was shown to be a viable method for KHIs [41][42]. **Table 2** summarizes the CMCs for the copolymers considered. Block copolymers with lower molecular weights and lower mole fractions of hydrophobic monomers were measured to have higher CMC [41][42]. This is an important consideration when designing new amphiphilic gas hydrate inhibitors.

Table 2. Critical micelle concentration (CMC) for all amphiphilic block copolymer gas hydrate inhibitors examined by Rajput et al. [41][42].

Block Copolymer	Molecular Weight	CMC
	kg/mol	×104 M
PS-PVA-40(0.05)	42.8	2.0
PPFS-PVA-40(0.05)	44.1	1.5
PS-PVP-20(0.10)	21.6	5.0
PPFS-PVP-20(0.10)	23.1	4.5
PS-PVCap(0.05)	77.1	2.9
PS-PVCap(0.10)	42.6	4.0
PS-PVCap(0.15)	23.9	7.0
PPFS-PVCap(0.05)	90.5	1.3
PPFS-PVCap(0.10)	46.2	3.7
PPFS-PVCap(0.15)	30.0	4.9
PPFS-PVCap(0.20)	23.8	6.0
PVCap-PVP(0.10)	53.1	45.9
PVCap-PVP(0.20)	28.0	58.0

Note: Block copolymer identifier: AA-BBB-XX(Y.Y); AA: hydrophobic monomer, BBB: hydrophilic monomer, XX: molecular weight of hydrophilic monomer in g/mol, Y.Y: mole fraction content of the hydrophobic monomer in the copolymer.

The mechanism of gas hydrate inhibition by polymers has not been completely characterized but remains best understood as an adsorption process. The inhibitor's hydrophilic groups adsorb on the surface of the growing hydrate crystal through hydrogen bonding, limiting its surface area available for gas mass diffusion, or the inhibitor's hydrophobic groups can interact with hydrophobic gas to limit their availability at the hydrate–liquid interface [74]. However, to further characterize the behavior of the liquid–hydrate interface in the presence of inhibitors, molecular dynamics simulations can offer an

insight into the molecular scale phenomena that occur. The initial efforts of researcher group to this end have been the characterization of the gas hydrate interface in the absence of inhibitors.

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