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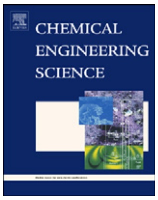

Surfactant effects on methane solubility and mole fraction during hydrate growth

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HIGHLIGHTS

- ► Measure the effects of SDS on hydrate growth in a stirred tank reactor.
- ► SDS has no effect on methane solubility but increases methane mole fraction.
- ► Increases in growth rate are attributed to the increase in methane mole fraction.
- ► Other factors, such as increased particle surface area, may also increase growth.

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ABSTRACT

Investigations are still ongoing to discover the mechanism by which surfactants promote hydrate growth. This paper investigates the effects of sodium dodecyl sulfate (SDS), a common surfactant for promoting hydrate growth, on methane solubility and mole fraction in the bulk liquid phase. Hydrates were formed in a stirred 600 cm^3 isobaric/isothermal reactor containing 343 cm^3 of liquid. Bulk solubility experiments under hydrate–liquid, liquid–gas, and hydrate–liquid–gas equilibria were performed at temperatures ranging from 275.1 K to 283.3 K and pressures ranging from 3049 kPa to 6500 kPa with pure water as well as SDS solutions. Kinetic experiments were also performed with water and 360-ppm solutions of SDS at temperatures of 275.1 K, 277.1 K and 279.1 K and pressures of 4545 kPa, 5180 kPa and 6080 kPa respectively. Measurements of the mole fraction of methane in the bulk liquid were taken at 0 s, 225 s and 450 s after hydrate nucleation. Experiments showed that SDS has no effect on bulk methane solubility at concentrations that significantly promote hydrate growth. SDS was found to increase methane mole fraction in the bulk liquid during hydrate growth following nucleation. Results were analyzed using the solubility model previously developed by Bergeron and Servio. The increase in methane mole fraction was found to be the major contributor to the increase in hydrate growth rate. It is estimated that other factors, such as changes in hydrate particle surface area, may also affect the growth rate and should be investigated further.

1. Introduction

Methane can form structure I crystalline gas hydrates when combined with water under suitable thermodynamic conditions (Sloan and Koh, 2008). These structures form naturally in ocean floors and permafrost regions and are estimated to represent an amount of organic carbon larger than all other sources on earth combined (fossil fuel, soil, peat and living organisms) (Suess et al., 1999). Methane hydrates could prove to be very useful in a multitude of industrial applications; one of the most notable is replacing liquefied natural gas transport in ocean tankers (Gudmundsson and Borrehaug, 1996).

The main challenge to using hydrates in industrial processes is their slow formation rates (Rogers and Zhong, 2000). Studies have shown surfactants, in particular sodium dodecyl sulfate (SDS), have a pronounced effect on hydrate formation (Kalogerakis et al., 1993; Zhong and Rogers, 2000). There is now much interest in understanding and characterizing the mechanism by which surfactants promote hydrate growth (Okutani et al., 2008). This information could help to guide the synthesis or selection of surfactants with properties better suited to promote hydrate growth.

It has been observed that the presence of surfactants in quiescent systems allows porous hydrate layers to form at the liquid–gas interface instead of a nonporous film (Mel'nikov et al., 1998; Kutergin et al., 1992). This increases hydrate growth by

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allowing water to be drawn up for hydrate formation rather than blocking gas and water from mixing (Okutani et al., 2008). In unstirred systems, it was initially thought that surfactants formed micelles above a certain critical concentration (CMC) and thus increased the solubility of the dissolved guest molecule (Zhong and Rogers, 2000). However, multiple studies have shown that SDS micelles are not present during hydrate formation and cannot form at the temperatures that were tested (Di-Profio et al., 2005; Watanabe et al., 2005; Zhang et al., 2007). Studies have also been performed on compounds that can form micelles under hydrate forming conditions and they have been shown to inhibit, or have little effect on, hydrate growth beyond the CMC (Di-Profio et al., 2007). Interest has recently turned to examining surfactant adsorption onto hydrates and to the effects this may have on growth (Del Villano and Kelland, 2009; Zhang et al., 2008). Two of the current theories for hydrate growth promotion include the formation of hydrophobic micro-domains near the hydrate surface that increase methane concentration, or a reduction in adhesion forces among hydrate molecules allowing for a larger particle surface area for hydrate growth (Lo et al., 2010).

Despite knowledge of these mechanisms by which surfactants may promote growth, it is still unclear as to which mechanism is most prominent in stirred systems. Many models have been developed for hydrate growth kinetics based on heterogenous reaction models (Clarke and Bishnoi, 2005; Englezos et al., 1987). Bergeron and Servio recently developed and used a model for hydrate growth in stirred systems that focuses on the liquid phase, eliminating the need to estimate the mass transfer at the gas–liquid interface, found as Eq. (1) (Bergeron and Servio, 2009; Bergeron et al., 2010; Bergeron and Servio, 2008).

$$\frac{dn}{dt} = \frac{V_L \rho_w}{MW_w} \frac{(x^l - x^{H-L})}{1/(\pi \mu_2 k_r)} \tag{1}$$

where V_L is the liquid volume in the reactor, ρ_w and MW_w are the mass density and molecular weight of the liquid water at reactor conditions. The driving force for this model is the difference between the mole fraction of the hydrate former in the bulk liquid (x^l) and its solubility under hydrate liquid equilibrium (x^{H-L}). Apart from this driving force, the model also relies on hydrate particle surface area, represented by the second moment (μ_2), as well as an intrinsic reaction rate constant to predict growth rates of hydrate particles in solution (k_r). This model could effectively describe many predicted mechanisms of hydrate growth promotion, such as an increase in the gas mole fraction in the bulk and/or at the hydrate–liquid interface or a change in solubility, all of which would affect the driving force. The area term could account for increases in hydrate interfacial area due to decreased adhesion forces between particles. Finally, any changes to the reaction mechanism would be represented by the intrinsic reaction kinetics term.

The purpose of the current study was to understand whether the bulk solubility of the hydrate former (methane in this case) changes with the addition of surfactants, and to investigate the effect of surfactants on mole fraction of the hydrate former during growth in a semi-batch stirred crystallizer. The goal of this is to clarify the main mechanism or mechanisms by which surfactants promote hydrate growth in stirred systems.

2. Materials and method

2.1. Experimental setup

A simplified diagram of the experimental setup containing an isothermal/isobaric semi-batch stirred tank crystallizer is shown in Fig. 1. Hydrates are formed in a 316 stainless steel crystallizer with a 20-MPa pressure rating and an internal volume of 600 cm^3. The crystallizer has two polycarbonate windows for visual inspection and is equipped with a MM-D06 magnetic stirrer from Pressure Product Industries. A Baumann 51000 control valve connects the stirrer to the reservoir in order to supply gas and maintain a constant pressure during hydrate formation. Reservoir and reactor biases are used to increase the accuracy of the pressure readings. To control temperature, the system is immersed in a temperature-controlled 20% ethylene glycol/water bath. Temperature is monitored using general purpose resistance temperature probes from Omega with an accuracy of ± 0.1 K. Pressure is monitored using Rosemount pressure transducers configured to a span of 0–14 MPa and differential pressure transducers configured to a span of 0–2 MPa, with an accuracy of $\pm 0.065\%$ of the given span. A National Instruments NI-DAQ 7 data acquisition system coupled with LabVIEW software is used to record all readings. The LabVIEW interface is set up to record the gas reservoir pressure and temperature, and uses the Trebble-Bishnoi equation of state to calculate the number of moles consumed at any given time. All materials are used as received from the suppliers. SDS is obtained from Sigma-Aldrich as a 99% pure A.C.S. reagent grade solid. Methane is obtained from MEGS Inc as 99.99% ultra high purity grade.

2.2. Procedure for measuring methane mole fraction during kinetic experiments

A more detailed procedure for solubility measurements during kinetic experiments can be found in a previous paper (Bergeron and Servio, 2009). Prior to injecting a new sample for experimentation, the reactor is washed six times with 360 mL of deionized water. Following this, 300 cm^3 of the desired solution of either deionized water or SDS is injected into the reactor, accounting for the 43-cm^3 holdup volume of water to get the desired concentration. After sample injection, the reactor gas is purged three times using methane by pressurizing to 1000 kPa and depressurizing to 100 kPa. Once thermal equilibrium is reached at the desired temperature, the crystallizer is pressurized to 1500 kPa above the three-phase equilibrium pressure (Frost and Deaton, 1946). The reactor temperature is allowed time to stabilize and then the reservoir control valve is set, the data acquisition system switched on, and the stirrer started at 750 rpm. The onset of hydrate growth is characterized by a

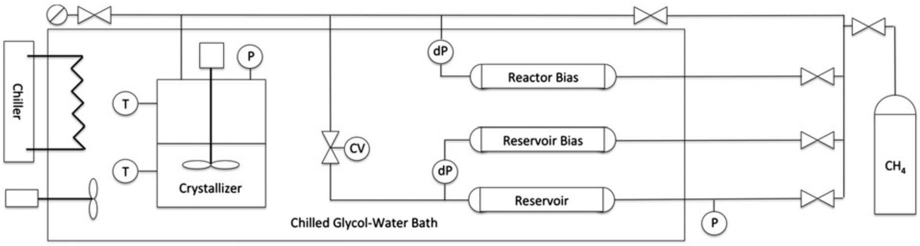

Fig. 1. Simplified schematic of the experimental setup.