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Assessing the performance of commercial and biological gas hydrate inhibitors using nuclear magnetic resonance microscopy and a stirred autoclave

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HIGHLIGHTS

- The results showed that MRI is an effective tool for the evaluation of the performance of KI.
- This technique was especially valuable to evaluate limitedly available biological KI's.
- MRI and gas uptake experiments showed the same trends in nucleation times.
- Microscopic (MRI) and macroscopic (gas uptake) experiments were in good agreement for growth assessment.

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ABSTRACT

The formation kinetics of methane/ethane/propane hydrate in the presence of kinetic inhibitors was investigated using ^{1}H nuclear magnetic resonance imaging (MRI) as well as a more-traditional method using a stirred autoclave. These studies were facilitated by fabricating a multi-drop insert for ^{1}H NMR micro-imaging, which allowed the comparison of the performance of microliter quantities of several inhibitors simultaneously and under the same conditions. Both methods showed that hydrate nucleation and growth were delayed significantly in the presence of inhibitors, which included two biological inhibitors (antifreeze proteins) and a commercial inhibitor. The results demonstrate that MRI is a useful tool for the visualization and evaluation of the performance of kinetic inhibitors on mixed gas hydrate formation. The MRI technique should prove especially valuable in the case of analysis of potential inhibitors, pre-commercialization, which are available in only limited quantities, such as biological inhibitors. This technique may also find utility in the exploration of differences in inhibitor performance, which may suggest distinct mechanisms of inhibitor action.

1. Introduction

The use of chemicals such as methanol and glycols for the prevention hydrate plug formation during oil and gas transport and in processing facilities has become an environmental concern. The handling, storage and recovery of these chemicals also poses potential environmental risks and can contribute to toxicity in the downstream process and water discharge. In addition, the economics of such practices are no longer attractive because of the high concentrations (>50%) of the chemicals employed to prevent the hydrate formation, especially in deep water and low temperature applications. Therefore industry has adopted new strategies, one of which is to use water-soluble polymers known as kinetic inhibitors (KIs) to delay the onset of hydrate formation and limit growth of hydrate. Anti-agglomerants (AAs) are a distinct class of inhibitors used to prevent agglomeration of hydrate particles [1]. The search for new KIs is ongoing in order to achieve improved performance and reduced costs. More recently there has been a focus on employing environmentally friendly, biological gas hydrate inhibitors such as antifreeze proteins (AFPs) [2–11].

Hydrate formation kinetics are commonly followed in the laboratory by monitoring gas uptake [1,12–17]. Recently, it has been recognized that such measurements represent the kinetic average of many local environments in a given sample [18]. This does approximate the bulk gas uptake curve, although only the local kinetic response can give detailed insight into nucleation and growth over the bulk sample. Moreover, the presence of KIs makes the hydrate formation process more challenging to analyze. As well as gas uptake, magnetic resonance imaging (MRI) has been used to monitor hydrate kinetics [18–25]. Despite its obvious benefits, however, there has been only limited use of this technique for

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studies of the dynamics of hydrate inhibition. However, MRI was successfully used to examine the fish, Type I AFP-mediated inhibition of the nucleation and growth of hydrate formed from either methane or propane [26]. To date, the use of MRI to investigate hydrate formation from gas mixtures in the presence of biological inhibitors has not been explored.

Therefore, the objective of the current work was to determine the utility of MRI analysis for the investigation of the performance of both chemical and biological inhibitors on mixed gas (methane/ethane/propane) hydrate nucleation and growth at the local, microscopic scale. These results could then be compared with the average, macroscopic scale data obtained by more-traditional gas uptake measurements. Validation of the kinetics of hydrate formation using MRI is important since this method is well suited to evaluate the performance of potential inhibitors, which might only be readily available at pre-commercial and investigative stage in small quantities, such as some biological inhibitors.

2. Experimental methodology

2.1. Materials

A commercial hydrate kinetic inhibitor H1W85281 (average molecular mass ~3 kDa, a proprietary commercial product of unknown composition) and two fish AFPs purchased from A/F Protein Inc. (Waltham, MA) were used: Type I AFP (AFP-I; average molecular mass: 3.3–4.5 kDa), purified from fish serum, and Type III AFP (AFP-III; Swiss Prot Database accession number P19414; average molecular mass: 7 kDa), purified after fermentation and secretion from recombinant *Saccharomyces cerevisiae* yeast cells. The methane (93%)/ethane (5%)/propane (2%) gas mixture (UHP grade) was supplied by Praxair Technology Inc.

2.2. MRI experiments

A 'droplet insert' (Fig. 1) for ^{1}H NMR micro-imaging was fabricated using Torlon (polyamide–imide (PAI); Boedeker Plastics, TX). Briefly, three stackable rounds (da – 6.98 mm, depth – 2.7 mm) each of with four depressions (dia – 1.46 mm) were supported by rod (dia – 3 mm, length – 25 mm). Samples (1 μL) were placed into the depressions using a micro-syringe and then transferred to a sapphire tube (dia – 7.5 mm; suitable for pressurizing in situ in the magnet up to ~35 MPa). The samples were pressurized to experimental pressure 9 MPa at 274 K. A Bruker Avance 200 NMR spectrometer was used to perform the ^{1}H NMR micro-imaging experiments using multi-scale spin echo pulse with Gaussian selective pulses, as described previously [18,26]. Two slices (250 μm thick, separated by 7.5 mm) were acquired simultaneously in planes perpendicular to the axis of the cell. The 192 × 192 acquisition matrix was extended to 256 × 256 for Fourier transformation. Multiple scans (8) were accumulated to increase the signal-to-noise ratio. The experimental arrangement is shown in Fig. 2. Hydrate formation kinetics were obtained by calculating the intensity of the droplets in the images as a function of time and over a predefined region of interest (using origin (8.1) software). The rate of hydrate formation was routinely calculated for 50 min intervals using the forward difference approximation [27].

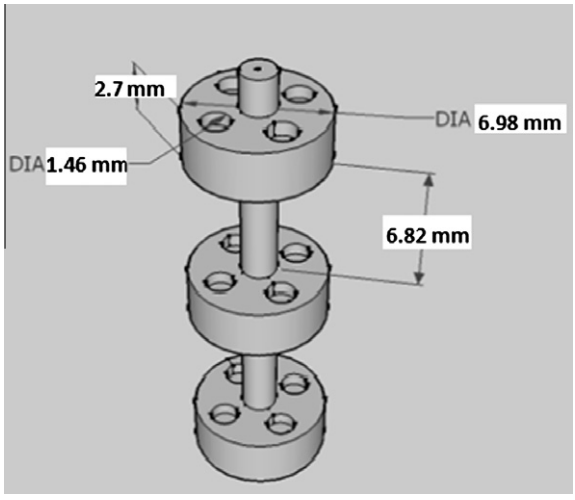

Fig. 1. Droplet insert used for magnetic resonance imaging experiments.

2.3. Gas uptake experiments

The apparatus and procedure has been previously described [11]. Briefly, the gas uptake experiments were conducted in a crystallizer (58 mL), loaded with the appropriate KI solution (10 mL). Time zero was designated at the point when the desired crystallizer temperature and pressure had been reached and the solution was stirred. All experiments were conducted at 275.15 K and 9 MPa, and using a batch protocol (constant temperature, with a fixed amount of aqueous solution and gas). Hydrate formation is associated with gas incorporation and the consequent drop in crystallizer pressure.

3. Results and discussion

3.1. Hydrate nucleation

Mixed gas (ethane/ethane/propane) hydrate nucleation in the MRI experiments was determined by the reduction in the liquid proton spin density. The time elapsed, from the initiation of the experiments to the reduction in spin density, was the induction time. Hydrate formation was rapid in the absence of inhibitors, and visually evident from the loss of intensity in the imaged bright areas, corresponding to the disappearance of liquid water as it was converted to solid hydrate (Fig. 3). When the normalized intensity (I_t/I_0: defined as the ratio of intensity at any given time I_t to the intensity at the start of experiment I_0) was plotted against time, the onset of hydrate nucleation in the presence of AFP-III and AFP-I was significantly delayed compared to the water samples (Table 1 and Fig. 4a). More specifically, hydrate nucleation was delayed by twofold in the presence of AFP-III (~60 min) and 10-fold by AFP-I (~300 min) compared to water (~30 min). Based on these results, AFP-I could be considered a more effective nucleation inhibitor compared to AFP-III. Moreover, hydrate nucleation did not occur even after 1100 min in the presence of HIW85281, indicating that the commercial inhibitor was the most effective in delaying the onset of hydrate nucleation.

Gas uptake experiments in a crystallizer monitored methane/ethane/propane hydrate formation by a sudden drop in pressure. There was a significant delay in hydrate nucleation in the presence of both chemical and biological inhibitors (Fig. 4b and Table 1). Similar to the MRI experiments, these results show that HIW85281 was most effective KI since it delayed hydrate nucleation by 265 min as compared to water, which nucleated in 1 min. Again, consistent with the MRI observations, AFP-I was a more effective inhibitor than AFP-III. AFP-III delayed nucleation by a factor of 8 and AFP-I delayed by a factor of 24.

Overall, the order of hydrate nucleation times remained as: water < AFP-III < AFP-I < HIW85281 no matter if monitored in 1 μL drops by MRI or in 10 mL batch gas uptake experiments.