Hydrate Shell Growth Measured Using NMR

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ABSTRACT: Benchtop nuclear magnetic resonance (NMR) pulsed field gradient (PFG) and relaxation measurements were used to monitor the clathrate hydrate shell growth occurring in water droplets dispersed in a continuous cyclopentane phase. These techniques allowed the growth of hydrate *inside* the opaque exterior shell to be monitored and, hence, information about the evolution of the shell's morphology to be deduced. NMR Relaxation measurements were primarily used to monitor the hydrate shell growth kinetics, while PFG NMR diffusion experiments were used to determine the nominal droplet size distribution (DSD) of the unconverted water inside the shell core. A comparison of mean droplet sizes obtained directly via PFG NMR and independently deduced from relaxation measurements showed that the assumption of the shell model—a perfect spherical core of unconverted water—for these hydrate droplet systems is correct, but only after approximately 24 h of shell growth. Initially, hydrate growth is faster and heat-transfer-limited, leading to porous shells with surface areas larger than that of spheres with equivalent volumes. Subsequently, the hydrate growth rate becomes mass-transfer-limited, and the shells become thicker, spherical, and less porous.

1. INTRODUCTION

Clathrate hydrates (hereafter referred to as hydrates) are ice-like crystalline compounds formed when hydrocarbon and water molecules come into contact under high pressures and low temperatures.¹ Hydrates were discovered by Sir Humphry Davy in 1810¹ and for a long period remained a laboratory curiosity. Nowadays hydrates are of interest across many diverse fields such as CO₂ sequestration, separation processes, natural gas transportation, and cool storage applications.² However, they are also a major concern for the oil and gas industry when they form and potentially block pipelines.³ Maintaining flow in such pipelines is obviously essential to production economics but also required to ensure safe operations and minimize the risk of environmental pollution.^{4,5}

In conventional oil transportation, where generally all three phases are present (water, oil, and (natural) gas), hydrates may form and agglomerate according to the conceptual model (Figure 1) proposed by Turner et al. in collaboration with J. Abrahamson.^{6,7} Initially, water droplets emulsify into the continuous oil phase because of shear in the pipeline, often assisted by other chemical agents in the oil phase.⁸ Hydrates will nucleate and grow at the water interface on the droplet surface, where there is also a supply of guest molecules (typically methane) dissolved in the oil, to form a hydrate shell around the droplet water core. Over time, the hydrate particles will agglomerate and can eventually jam and plug the pipeline.^{1,9,10} Flow assurance engineers seek to avoid this situation by either preventing hydrate formation conditions from occurring in the pipeline or, when this is unavoidable, by actions based on a quantitative understanding of the mechanisms by which hydrates grow and form plugs.¹⁰

Generally, industry aims to completely prevent hydrate formation by injecting sufficient quantities of inhibitor

chemicals such as monoethylene glycol (MEG) or methanol; however, such an approach becomes increasingly expensive the deeper and further offshore the hydrocarbon exploration and transportation occurs.¹¹ Accordingly, industry is now moving from complete hydrate avoidance to a risk management approach (that may involve partial inhibition).⁴ However, there are still significant knowledge gaps relating to how hydrates form, agglomerate, and plug pipelines, as well as with respect to the exact mechanisms by which various forms of hydrate inhibition, that target these phenomena, operate.^{12,13} Studying these phenomena at a microscopic level, such as measuring adhesion/repulsion forces between hydrate particles and understanding the chemistry between inhibitors and hydrates at the interfacial level, is central to ongoing research efforts aimed at addressing these knowledge gaps (see, e.g., ref 9).

Experimental methods used for characterizing hydrate shell growth around water droplets, as schematically shown in Figure 1, include X-ray and neutron diffraction,¹⁴ Raman spectroscopy,¹⁵ optical spectroscopy¹⁶ and infrared spectroscopy.¹⁷ Conventionally hydrate shell growth kinetics have been studied by monitoring the gas consumption in a pressure cell. Such experiments, however, do not quantify the morphology of the growth.¹⁸ Since the hydrate shell is visually opaque, most of the previously mentioned techniques are limited in their ability to quantitatively measure shell growth in detail, particularly with respect to the shell interior. Alternative methods of probing hydrate shell growth which, in principal, can measure the morphology include differential scanning calorimetry (DSC) 79

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Figure 1. Conceptual picture of hydrate formation in an oil dominant multiphase flow line. Adapted with permission from ref 6. Copyright 2006 Colorado School of Mines. Hydrate shell formation, indicated as white coloring, occurs around emulsified water droplets in the growth and agglomeration stages.

80 and nuclear magnetic resonance (NMR).¹⁹ The use of NMR
81 techniques to probe hydrate shell growth is the focus of the
82 work presented here.

83 NMR provides a noninvasive technique that does not require
84 optical access; it can be readily applied to determine droplet
85 size distributions in emulsions,^{20,21} the precursor micro-
86 structure to shell growth. This attribute has been used by
87 Aichele et al.¹⁹ to study subsequent hydrate growth within
88 water-in-oil emulsions in which hydrates were formed using
89 methane. The NMR methodology employed relied on the
90 quantification of restricted molecular water self-diffusion via the
91 application of NMR pulsed field gradient (PFG) techniques.
92 They applied these techniques to consider whether hydrate
93 formed via the shell model or via the complete conversion of
94 discrete droplets above a critical diameter (the threshold
95 model). Their data were shown to be consistent with the shell
96 model and in accordance with other evidence in the literature.¹
97 Restriction of (water) molecular self-diffusion within the
98 emulsion droplets is the physical phenomenon that enables
99 quantification of the droplet size distribution (DSD) in an
100 emulsion using PFG techniques. This restriction, however, can
101 result from the original emulsion droplet surface, or, as is the
102 case for the work presented here and by Aichele et al.,¹⁹ the
103 inner surface of the hydrate shells. Thus, PFG NMR allows
104 probing of the inner water content of the hydrate encrusted
105 droplets.

106 A number of other relevant studies have sought to use NMR
107 techniques to measure hydrate formation. Gao et al.²² studied
108 the formation of hydrates in a THF and D₂O system. As D₂O
109 does not provide a ¹H NMR signal, they were able to
110 quantitatively monitor the disappearance of the THF signal
111 over time as it was converted into hydrate. Melnikov et al.²³
112 used ¹H NMR to study phase transformations of water in gas
113 hydrate systems including their metastable states at temper-
114 atures below the ice point for a Freon–water hydrate system.
115 Majid et al.²⁴ used NMR relaxation methods to measure
116 emulsion droplet size distributions which were a precursor to
117 hydrate formation.

118 Much of our understanding about hydrate formation and
119 growth has been derived from visual measurements in optically
120 transparent systems. Chen et al.²⁵ observed hydrate formation
121 on suspended gas bubbles in a counterflowing water column,
122 where mobile hydrate plates at the gas–water interface were
123 found to precede rapid growth of the hydrate shell.
124 Quantitative visual observations, collected over the past 2
125 decades, have generally investigated the formation of hydrate
126 films across flat horizontal interfaces between water and the
127 respective hydrocarbon. Hydrate film thickness and propaga-

tion rate can be measured with different techniques, in
particular laser interferometry, micrometer measurements, and
visual microscopy. Taylor et al.²⁶ presented visual measure-
ments of cyclopentane hydrate film thickness with the help of
digital video microscopy; this film thickness increased from 14
to 34 μm over a subcooling range of 4–10 K. The film required
200 min to reach a steady-state condition. Parallel data for
methane hydrate films, which increased in thickness from 18 to
46 μm over a subcooling range of 3.5–7.5 K, were broadly
consistent with film thickness estimates of 10–52 μm from
Makogon et al.²⁷ and visual observation of 8–48 μm hydrate
film growth on a suspended gas bubble by Li et al.²⁸ Wu et al.²⁹
estimated hydrate film thicknesses of 1.3–25 μm for a
methane–propane mixed gas hydrate system observed with a
HP-Video cell.

Following formation of this initial hydrate film (which in the
case of water emulsion droplets will be a hydrate shell),
continued hydrate growth is limited by mass transport of the
guest species and/or water across the hydrate shell lattice.⁷ This
continued hydrate growth is a critical parameter for estimating
the total hydrate fraction, residual water, and hence droplet
cohesion for any hydrate residence times extending to weeks;
for example during unplanned shut-ins (where production is
halted) of oil production lines. The current study represents the
first effort to quantify this continued hydrate growth with
NMR, a noninvasive technique that is not constrained by the
opaque hydrate shell on the emulsion droplets.

In this work, NMR was used to study the formation and
subsequent growth of cyclopentane hydrate films on water
droplets dispersed in (excess) cyclopentane. The kinetics of
water consumption as cyclopentane hydrate formed (and the
resultant hydrate shell grew on the water droplets) was
measured using two independent NMR signal relaxation
measurements under hydrate-forming conditions over several
weeks. Simultaneously the diameter of the water core within
the hydrate shell was measured using PFG NMR techniques.
Thus, we extend beyond the study of Aichele et al.,¹⁹ that used
PFG NMR to confirm the formation of a hydrate shell on the
emulsion droplets, to quantify the evolution in the water core
diameter as hydrate film growth occurs. We are also able, for
the first time, to infer the water core diameter from the NMR
relaxation measurements. As detailed later, comparison of the
water core diameters as measured by PFG NMR and NMR
relaxation measurements respectively allows the morphological
assumption of a perfect sphere for the water core to be tested.
All NMR measurements were performed using a benchtop
comparatively low field and, hence, more readily accessible
NMR apparatus.

2. BACKGROUND

2.1. Relevant NMR Theory. NMR relaxation refers to the process through which all of the nuclear spins in a sample return to thermodynamic equilibrium (the lowest energy state)³⁰ following excitation. In NMR two major relaxation processes can occur: longitudinal relaxation (T_1) and transverse relaxation (T_2).³¹ The longitudinal relaxation time is the time needed for the spins to realign with the axis of the external magnetic field and give up all their energy to the lattice in order to restore thermal equilibrium. To determine the T_1 relaxation time, we used the saturation recovery method, which can be described by

$$S(t) = S_\infty(1 - \exp(-t/T_1)) \quad (1a)$$

where S is the signal measured at time t and S_∞ is the signal intensity at equilibrium. The transverse relaxation time is the time characteristic in which the spins dephase with respect to one another due to molecular interactions or magnetic field inhomogeneities. It can be described by

$$S(t) = S_0 \exp(-t/T_2) \quad (1b)$$

where S is the signal measured at t and S_0 is the signal intensity at time 0. In the case of a porous environment, for example a saturated rock sample, relaxation times for contained fluid (usually water) give important information about porosity, surface-to-volume ratio, permeability, formation factor, tortuosity, pore size distribution, and pore connectivity.³² This is possible because the relaxation times are sensitive to both molecular motion and pore geometry. Additional information can also be extracted by performing such relaxation measurements as a function of resonance frequency using fast field cycling techniques.³³ For a porous medium the dimensions of the pores are related to relaxation times by the Brownstein–Tarr equation.^{34,35} The T_1 and T_2 relaxation times of the contained fluid can be written as

$$\frac{1}{T_1} = \frac{1}{T_{1,\text{bulk}}} + \rho_1 \frac{S}{V} \quad (2a)$$

$$\frac{1}{T_2} = \frac{1}{T_{2,\text{bulk}}} + \rho_2 \frac{S}{V} + \frac{D}{12}(\gamma G t_E)^2 \quad (2b)$$

where T_1 and T_2 are the apparent relaxation times (s), $T_{1,\text{bulk}}$ and $T_{2,\text{bulk}}$ are the relaxation times in a nonrestricted environment (s), ρ_1 and ρ_2 are the surface relaxivities ($\mu\text{m/s}$), S/V is the surface-to-volume ratio (m^{-1}) of the confining medium, D is the diffusion coefficient (m^2/s) of the contained fluid, γ is the gyromagnetic ratio (MHz/T), G is the background magnetic field gradient strength (T/m), and t_E is the echo time (s). The Brownstein–Tarr theory equations (eq 2) are strictly only valid for the fast diffusion limit ($\rho a/D \ll 1$), this was found to be true for the vast majority of the acquired data with $(\rho a/D)$ always < 1 . If t_E is sufficiently short, then the third right-hand-side term of eq 2b can be neglected and the relaxation is dominated by just surface relaxation. In this case, the relaxation rate of a fluid in a pore is given by³⁶

$$\frac{1}{T_{1,2}} = \frac{1}{T_{1,2,\text{bulk}}} + \rho_{1,2} \frac{S}{V} \quad (3)$$

In the cases when the confining geometry of the fluid (the pore) is a perfect isolated sphere, such as an emulsion droplet, $S/V = 3/a$ where a is the sphere radius. Probability distributions of T_1 or T_2 were determined using standard

regularization techniques, the specific details of which are provided by Mitchell and Chandrasekera.³⁷

The measurement of unrestricted self-diffusion of molecules in a liquid by PFG NMR methods was first demonstrated by Stejskal and Tanner.³⁸ The method essentially relies on signal attenuation due to random motion (diffusion) of the molecules between two imposed magnetic field gradients. The resultant NMR signal loss ($I = S/S_0$) is described by

$$I = \exp\left(-D(\gamma\delta g)^2\left(\Delta - \frac{\delta}{3}\right)\right) \quad (4)$$

where D is the self-diffusion coefficient of the relevant molecules and Δ , δ , and g are the temporal duration between application of the two magnetic field gradients, the duration of a single magnetic field gradient application, and the strength of the magnetic field gradient, respectively. γ is the gyromagnetic ratio of the spin; the ^1H nucleus, which has $\gamma = 2.68 \times 10^8 \text{ T}^{-1} \text{ s}^{-1}$, was used exclusively in the work presented here. I is thus measured as a function of g , δ , or Δ enabling the extraction of D via application of eq 4. The NMR pulse sequence most commonly employed to achieve this with respect to emulsion characterization is based on a stimulated echo signal, which will be detailed in Materials and Methods.

In the case of restricted self-diffusion inside a spherical geometry (e.g., an emulsion droplet, or in the hydrate water core), the NMR signal attenuation can be approximated as³⁹

$$\ln I(D, a, g, \delta) = -2\gamma^2 g^2 \sum_{m=1}^{\infty} \frac{1}{\alpha_m^2 (\alpha_m^2 a^2 - 2)} \left[\frac{2\delta}{\alpha_m^2 D} - \frac{\psi}{(\alpha_m^2 D)^2} \right] \quad (5a)$$

$$\psi = 2 + \exp^{-\alpha_m^2 D(\Delta - \delta)} - 2 \exp^{-\alpha_m^2 D\Delta} - 2 \exp^{-\alpha_m^2 D\delta} + \exp^{-\alpha_m^2 D(\Delta + \delta)} \quad (5b)$$

where α_m is the m th positive root of the equation:

$$J_{5/2}(\alpha\alpha) - \frac{1}{\alpha\alpha} J_{3/2}(\alpha\alpha) = 0 \quad (5c)$$

J_k is the Bessel function of the first kind of order k , and a is the droplet radius. Equations 5 assume that the NMR signal phase (φ) distribution is a Gaussian shape. An alternative to eqs 5 exists in which it is assumed that the duration of the applied magnetic field gradient pulse, δ , is infinitely short.⁴⁰ More recently, however,⁴¹ it was demonstrated that the use of the block gradient pulse (bgp) approximation method to describe restricted diffusion inside spherical droplets (emulsion droplet sizing) offered improved accuracy compared to the assumption of a Gaussian phase distribution or an infinitely short δ over all practical considerations of experimental parameter space. The bgp method is based on the generalized gradient waveform set of methods,^{42–44} in which an eigenfunction expansion is used to solve the Bloch Torrey equation in the presence of a piecewise-constant gradient waveform.⁴⁵ The Bloch Torrey equation is reposed, for self-diffusion in a spherical emulsion geometry, in (Laplace operator eigenbasis) matrix form as

$$S(\tilde{t}) = \mathbf{v}^\dagger \left(\prod_{k=1}^{N_c} e^{[-\Lambda + i(\tilde{\gamma}_k \cdot \tilde{z})\mathbf{Z}]\tilde{t}_k} \right) \mathbf{v} \quad (6)$$

where for reflective emulsion boundary with no surface relaxation $v_j = \delta_{j1}$, $\tilde{t} = Dt/a^2$, $\tilde{\gamma} = -c\gamma a^3$, and $\Lambda_{jk} = \alpha_{nm}^2 \delta_{jk}$ while $\mathbf{Z}$ for a sphere is given analytically by Grebenkov.⁴⁵ Here δ is the Kronecker delta. Note that Λ and $\mathbf{Z}$ respectively represent the evolution of magnetization due to diffusion and

gradient dephasing. Expansion of eq 6 for the stimulated echo PFG pulse sequence used here allows the NMR signal attenuation (I) to be expressed as

$$I = \frac{\mathbf{v}^\dagger e^{(-\Lambda + i(\tilde{\gamma} \cdot \tilde{z})\mathbf{Z})\delta} e^{-\Lambda(\Delta - \delta)} e^{(-\Lambda + i(\tilde{\gamma} \cdot \tilde{z})\mathbf{Z})\delta} \mathbf{v}}{\mathbf{v}^\dagger e^{-\Lambda(\Delta + \delta)} \mathbf{v}} \quad (7)$$

where the only free parameter is the droplet size a . Greater details regarding the mathematical derivation can be sourced from Grebenkov⁴⁶ and our implementation for emulsion droplet sizing, as was exclusively employed in the work presented here, is detailed in Lingwood et al.⁴¹

Most emulsions consist of a distribution of droplet radii, $P(a)$ (number based), meaning the measured signal is described by the following integral:

$$I(D, g, \delta) = \frac{\int_0^\infty a^3 P(a) I(D, a, g, \delta) da}{\int_0^\infty a^3 P(a) da} \quad (8)$$

where $I(D, a, g, \delta)$ is the signal attenuation function described by eq 7. The extraction of $P(a)$ from eq 8 is both an ill-conditioned matrix inversion (when tackled analytically) and an unstable minimization problem (when tackled numerically). Previously we have demonstrated⁴⁷ the use of the Tikhonov regularization method to numerically invert eq 6 with generalized cross-validation (GCV) used for regularization parameter selection; this does not require any assumption regarding the droplet size distribution shape.

2.2. Relevant Hydrate Theory. Clathrate hydrates are crystalline inclusion compounds, where molecular water cages surround lighter hydrocarbon species.¹ Two different cubic hydrate structures are commonly found: I and II. Structure I hosts smaller guest molecules and is the structure found most commonly in the natural environment, whereas structure II contains cages that can host larger guest molecules and is predominantly found in oil and gas production systems.⁴⁸ This investigation used cyclopentane as an ambient pressure structure II former that is immiscible with water. Consequently, cyclopentane hydrate formation is generally confined to interfaces between hydrocarbon and aqueous phases, which together with the fact that it forms structure II, makes it a closer analogue to the hydrates that form in oil and gas pipelines (as opposed to THF which is often used in ambient pressure hydrate studies). Structure II cyclopentane hydrates contain 16 small 5^{12} cavities (pentagonal dodecahedron) and 8 large $5^{12}6^4$ cavities (hexakaidecahedral), with 136 water molecules per unit cell.⁴⁸ Cyclopentane hydrate has a relatively high hydrate-forming equilibrium temperature of 7.7 °C at atmospheric pressure.^{49,50}

Hydrate formation, in general, occurs in two steps: (1) nucleation and (2) growth. Although hydrate growth occurs at any temperature below the hydrate equilibrium temperature, operating at such thermodynamically favorable conditions will not guarantee the instantaneous nucleation of hydrates.^{26,51,52} Nucleation time (t_{nuc}) is the time interval between the establishment of hydrate stability conditions and the formation of the first hydrate clusters. In literature, there is a large variability in t_{nuc} .⁵³ Sloan and collaborators⁵⁴ note that this is an indication that t_{nuc} is dictated by a stochastic process, particularly for smaller sample volumes and lower subcoolings.⁵⁵ Furthermore, the “type” of water employed for hydrate formation in a static system (without flow) was also found to play an important role.⁵⁶ Thawed ice produced the shortest

nucleation time. Numerous studies have attributed this observation to the fact that the ice–hydrocarbon–aqueous interface between phases acts as a heterogeneous nucleation site.^{1,55,57,58} The incipient water from melted ice still contains residual structure that it is hypothesized to provide a template to form the water cage structure of a hydrate.¹ If the study of hydrate growth is the main objective, then promoting hydrate nucleation is advantageous and, therefore, the use of recently thawed ice (as is the case for experiments performed in the work presented here) is convenient.

Following nucleation of hydrate at the interface between two immiscible phases, hydrate film growth occurs at a rate that is set initially by heat-transfer limitations. Visual methods have been used to study the nature and morphology of this growth along planar interfaces and across the exterior surface of suspended droplets or bubble until a complete shell is formed, after which time the amount of information extractable becomes limited. Using data measured by Uchida et al.,⁵⁹ Mori proposed a model for hydrate film growth which related the product of the initial film’s lateral growth rate and the thickness to the enthalpy of formation, a convective heat-transfer coefficient and a power law dependency on the system subcooling.⁶⁰ This applicability of this heat-transfer-limited growth model to the initial growth of planar hydrate films was validated in 2007 by the experiments of Taylor et al.²⁶ who quantified both the film propagation rate and thickness as a function of time for both cyclopentane and methane hydrates. While the initial film thicknesses were about 12 μm for cyclopentane hydrates, these increased to final values of about 25 μm for subcoolings around 8 K over a period of 200 min. For methane hydrates at this subcooling, the steady-state thicknesses reported by Taylor et al.²⁶ were 50 μm , which was consistent with the results of other measurements of planar interfaces.^{27,28} However, as pointed out by Ohmura et al.,⁶¹ the initial phase of hydrate film growth is sensitive to the system geometry (e.g., shell vs film) because this affects the nature of the free-convective motion of the water sweeping the growing hydrate film and determining the magnitude of heat transfer possible.

Genov et al.⁶² proposed that the initial phase of rapid growth gave rise to a porous hydrate shell that would subsequently allow for reasonable rates of mass and heat exchange between the phases. Chen et al.⁶³ visually observed the formation of a porous hydrate shell at the methane–water interface in a high-pressure water tunnel, similarly concluding that the shell did not introduce a significant barrier to mass transport between the continuous phases in the early stages of growth. Following the initial rapid phase of heat-transfer-limited growth, which lasted about 10 min, Taylor et al.²⁶ observed growth occurring at a much slower rate as the cyclopentane hydrate film thickened to its steady-state value over several hours. This second phase growth is mass-transfer-controlled and depends not only on the diffusivity of the hydrocarbon molecules through the film but also on the porosity of the hydrate film.⁶⁴ Rao et al.⁶⁵ studied the deposition and porosity of a methane hydrate film on a cold steel surface, reporting porosity values above 75% for the first 20 h of growth; after 75 h of annealing, however, the film porosity decreased to approximately 5%. For spherical interfaces, as the hydrate shell grows thicker and/or its porosity is reduced, mass-transfer resistance also increases and the growth rate of the hydrate shell layer consequently will decrease. This effect is consistently observed across many studies.^{18,66–69} Extrapolating from their measurements of

Figure 2. Modified SSE PFG pulse sequence which is able to differentiate between the water and the oil (cyclopentane) signal based on adequate differences in the T_1 relaxation parameter. This was enabled by dissolving a Gd complex in the cyclopentane prior to use.

Figure 3. Results of the T_1 relaxation experiment: (a) T_1 distribution curves, showing the two sets of peaks for cyclopentane and water, respectively; (b) water mole fraction obtained for two independent experiments showing the reduction in water mole fraction as a thicker hydrate shell is formed.

planar hydrate films, Taylor et al.²⁶ hypothesized that full conversion of water contained within a spherical hydrate shell might require time scales on the order of tens of hours.

3. METHODOLOGY

3.1. Materials and Methods. To prepare cyclopentane hydrates, sieved ice particles (made from deionized water) with nominal diameters between 150 and 250 μm were mixed with excess cyclopentane at -20°C . A reduced selection of experiments was also performed with ice particle nominal diameters between 75 and 150 μm and below 75 μm , respectively. As discussed earlier, the use of thawed ice promotes a higher degree of initial molecular water ordering and contributes to faster hydrate growth.⁵⁵ The required sieving of pulverized ice was performed in an appropriately cold environment (the sieves being cooled with liquid nitrogen), after which both the ice particle and the cyclopentane were separately stored at -20°C using a Haake Phoenix cooling bath. The cyclopentane and the ice particles were rapidly mixed in precooled 9 mm inner diameter NMR glass test tubes that were subsequently closed, then heated to 1°C , and maintained at room pressure. This storage temperature was above the melting temperature of ice but below the cyclopentane equilibrium temperature of 7.7°C at 1 bar, which meant a subcooling of 6.7°C . The NMR test tubes were then placed in the benchtop NMR spectrometer (detailed later) in a 1°C environment; relaxation and diffusion experiments (also detailed later) were performed daily for a period of at least 14 days. In this manner we were able to monitor the gradual hydrate shell thickening following initial rapid hydrate shell formation.

All NMR measurements were performed using a commercially available benchtop NMR Minispec mq Bruker spectrometer, with a ^1H resonance frequency of 20 MHz.⁷⁰ The Bruker Minispec features a strong pulsed gradient (4 T/m) for PFG purposes, is able to accommodate 10 mm (outer diameter) NMR tubes, and provides sample temperature control which was kept constant at 1°C during all experiments. For the NMR relaxometry measurements, standard saturation recovery and CPMG^{71,72} pulse sequences were employed to obtain the T_1 and T_2 relaxation time distributions, respectively.

The NMR pulse sequence used for all self-diffusion measurements was the modified stimulated spin echo (SSE) PFG, as shown in Figure 2. Since the Bruker Minispec has no spectral resolution, it is not possible to directly differentiate the NMR signal from the water and cyclopentane phases, respectively. Consequently a 180° radio frequency (rf) pulse is conventionally inserted at the pulse sequence initiation, followed by a time delay equal to the null point of the oil signal ($0.693T_{1,\text{oil}}$). This pulse sequence has previously been employed to determine the size distribution of water-in-crude oil emulsions employing the same NMR hardware.⁷³ The relaxation times (both T_1 and T_2) for cyclopentane and water are, however, very similar (the T_1 at 1°C for water is 1.5 s; for cyclopentane it is 1.8 s); thus selective suppression-nulling of the cyclopentane signal using the SSE PFG pulse sequence is not possible. Hence, in order to reduce the relaxation time of the cyclopentane, we employed a paramagnetic gadolinium complex that was soluble only in the cyclopentane. This complex was gadolinium tetramethyl heptanedionate (Gd(III) TMHD), which was purchased from Multivalent Laboratory. It is not soluble in water but presents a solubility of 2.9 mmol/L in hexane⁷⁴ and a similar solubility in cyclopentane. Such paramagnetic compounds are generally used in MRI as contrast agents to better differentiate between tissues.⁷⁵ In our case, we dissolved 0.6% (w/w) Gd(III) TMHD salt into the cyclopentane prior to mixing of the cyclopentane and any ice; the Gd complex remained in solution at all temperatures considered. This served to reduce the T_1 relaxation time for the cyclopentane from 1.8 to 0.35 s, enabling ready differentiation of the water and cyclopentane contributions to acquired relaxation distributions, as well as effective suppression-nulling of the cyclopentane NMR signal during PFG measurements.

With reference to Figure 2, the observation time (Δ) used in all experiments conducted here was 180 ms, the gradient pulse length (δ) was 2 ms, and the gradient strength (g) was increased from 0 to 0.2 T/m in 16 increments. Inversion of the acquired data to produce the emulsion droplet size distributions was performed using eq 8 and the bpg method detailed earlier.

Figure 4. Results of the T_2 relaxation experiment for ice particles of nominal diameter 150–250 μm : (a) T_2 distribution curves, showing the two separate group of peaks for cyclopentane and water, respectively; (b) water mole fraction calculated by integrating the relaxation peaks for water and cyclopentane over time and adjusting for ^1H density for three different ice particle sizes.

Figure 5. (a) Droplet size distribution (DSD) obtained with the PFG NMR diffusion experiments. A decrease in the droplet mean value is observed over 9 days, corresponding to the shrinking of the water core. (b) Comparison between the mean droplet size obtained by self-diffusion and T_2 relaxation measurements respectively for two independent experiments. The solid lines are the predicted change in droplet size from day 2 onward, based on the residual water content measured and reported in Figure 4b, using the diameter, as measured using relaxation measurements, on day 2 as an anchor point.

4. RESULTS AND DISCUSSION

4.1. Hydrate Growth Kinetics. A set of sample T_1 relaxation data is presented in Figure 3a as a function of time following thawing of the ice content in the sample at 1 $^{\circ}\text{C}$, as detailed previously. The T_1 value for water is ~ 1.5 s, which corresponds to the right group of peaks in Figure 3a, and the T_1 value for cyclopentane is ~ 350 ms, which corresponds to the left group of peaks in the same figure. The addition of the Gd complex clearly facilitates the quantitative differentiation of the cyclopentane and water contribution in these relaxation distributions. Over a period of 7 days, the water peak shifted to the left and diminished in intensity, while there was comparatively little change in the cyclopentane peak. The shift to lower values for the water peak reflects the fact that water-occupied domains decreased in size consistent with eq 3; the reduction in intensity reflects the reduction in the liquid water content of the sample as it converted to hydrate, which is NMR invisible for these measurements. The small reduction in the cyclopentane reflects changes in the cyclopentane content in the detection field of view as well as by consumption to form hydrate. It is important to note, however, that the cyclopentane is in excess and that 13.5 mol of water are consumed per mole of cyclopentane due to selective guest occupancy in the large cage of structure II.¹

Using the areas under the peaks and correcting for differences in the relative ^1H density between water and cyclopentane, it is possible to calculate the water mole fraction

in the detected sample volume—its evolution with time following ice thawing at 1 $^{\circ}\text{C}$ is presented in Figure 3b. An independent repeat experiment is also shown indicating the reproducibility of the observed hydrate growth kinetics. The “noise-like” variation evident in the data in Figure 3b is a combined consequence of noise in the acquired NMR data and the required numerical data inversion employing the regularization techniques in eq 8 to produce the probability distributions presented in Figure 3a.

The corresponding T_2 relaxation time distribution data for the preceding experiments are shown in Figure 4a, along with the resultant water mole fractions in Figure 4b determined as a function of time following ice thawing. The water and cyclopentane peak groups are distinct in Figure 4a, and their general behavior is consistent with that observed based on T_1 measurements (in Figure 3). Also shown in Figure 4b are the data corresponding to reduced ice particle diameters of 75–150 and <75 μm . The hydrate formation kinetics (shown in Figure 4b) are very consistent with that shown in Figure 3b. The acquired NMR data are considerably less noisy than those used to construct Figure 3 and hence has higher reproducibility as revealed by the independent experiment also shown in Figure 4b. Since T_2 measurements can be performed more rapidly, which allows for more signal averaging, they will exclusively be used in the future for such hydrate growth kinetic measurements. Also evident in Figure 4b is a distinct change in hydrate formation rate between day 1 and day 2. This we speculate is a

consequence of a transition from heat-transfer-limited growth to mass-transfer-limited growth, for which there is considerable literature evidence, as discussed earlier. Because the initial ice particles size is reduced, there is a reduction in the residual water content on day 1. As discussed later, this is consistent with the initial rapid formation of a hydrate film; assuming a constant thickness for such a film would reduce the residual water content as ice particle size is reduced. Subsequent kinetics from day 2 onward do not show any obvious trend with initial ice particle size.

From the daily NMR diffusion experiments (using the pulse sequence presented in Figure 2) we obtained the droplet size distribution (DSD) for the water cores inside the hydrate shells, which are presented in Figure 5a as a function of time post-ice-thaw. As discussed earlier, hydrate shells have been observed in the literature to form relatively quickly with a thickness of up to $\sim 50\ \mu\text{m}$. Our initial ice particles were between 150 and $250\ \mu\text{m}$ in diameter, thus we would expect that the initial water core size distribution following initial hydrate shell formation would approximately be between 50 and $150\ \mu\text{m}$ (a total reduction in diameter of $100\ \mu\text{m}$). This size range is broadly what is observed in Figure 5a for the first day. On day 1, a second peak in the DSD distribution is also observed at in excess of $400\ \mu\text{m}$ —this we attribute to free water, since $400\ \mu\text{m}$ is beyond the upper detection limit of the method. This small free water peak was consistently observed in repeat experiments but always disappeared by day 2, presumably having been converted into hydrates. There is a significant decrease in water core diameter between days 1 and 2 followed by a much more gradual reduction over subsequent days. This rapid initial consumption is consistent with results from previous studies for other hydrate systems (see, e.g., refs 26, 62, and 65).

From these distributions we extracted the mean values for the water core sizes for each day; the results are plotted in Figure 5b. An initial rapid reduction in the mean core size is observed followed by a very subtle reduction. There appears to be a steady-state value around $30\text{--}40\ \mu\text{m}$ (corresponding to a hydrate shell thickness between 55 and $110\ \mu\text{m}$) over the time scale studied. From the T_2 relaxation experiments we were also able to obtain the mean droplet size using eq 3. This required multiple comparisons of the equilibrium water core size (as measured using PFG techniques) with relaxation measurements in order to determine the required surface relaxivity, ρ . A value of $12\ \mu\text{m/s}$ was produced, which is consistent with the value $15\ \mu\text{m/s}$ reported for ice–water surfaces obtained via NMR studies.⁷⁶ Using this value, the mean droplet size distribution is plotted in Figure 5 against the PFG NMR data for two independent series of experiments. The agreement between these two distinct measurement protocols—PFG NMR measurement of restricted self-diffusion and NMR T_2 relaxation measurements—is adequate post the first day for both independent sets of experiments.

The day 1 results for experiments 1 and 2 shown in Figure 5b are in disagreement; however, this is no doubt affected by the comparatively rapid change occurring at this temporal point relative to the temporal resolution of the overall data acquisition (~ 1 day). Between experiments 1 and 2, the order of measurement (PFG and T_2 relaxation) was reversed; however, the results consistently show on day 1 that the T_2 prediction of water core size is significantly smaller than the PFG-based measurement. The T_2 measurement is sensitive to the S/V ratio of the confined water core and strictly can only be compared with the PFG-derived mean droplet size, by

assuming that the water core is a perfect sphere. The difference between the PFG-derived and T_2 -relaxation-derived mean droplet sizes implies this is not the case on day 1. As discussed earlier, the collective studies of Genov et al.,⁶² Chen et al.,⁶³ and Rao et al.⁶⁵ of flat hydrate films or shell exteriors indicate that the initial hydrate film is highly porous, with the porosity reducing significantly subsequently over time. Such a porous hydrate film would result in a larger S/V ratio with respect to the relaxation measurements and, consequently, the observed smaller “apparent water core diameter” ($\propto (S/V)^{-1}$) measured relative to the diffusion measurement. The diffusion measurement is more immune to the actual S/V ratio (provided the porous hydrate film presents a sufficiently low permeability) and in this case is dictated more by the actual dimension of the water core within the hydrate shell. Also shown in Figure 5b by the solid lines is the prediction of the evolution in droplet diameter from day 2 onward based on the residual water amount extracted from Figure 4b as a function of time. This assumes the core to be a sphere and also pivots off the diameter for day 2 and hence assumes it to be correct. This is in excellent agreement with the diameters measured on days 3–9.

Thus, the evidence suggests that the initial hydrate shell is a high S/V porous film. This film porosity is, we hypothesize, significantly reduced by day 2, and the assumption of a spherical water core is supported by the congruence of all independently measured data from this temporal point onward. Future work will focus on increasing the frequency of these NMR measurements (requiring the employment of a higher specification high-field magnet) so as to interrogate the initial shell formation more thoroughly, as well as focusing on methane hydrates employing appropriate NMR-compatible high-pressure apparatus.

5. CONCLUSIONS

We have shown the effectiveness of using low-field NMR to measure directly the water core size enclosed within a cyclopentane hydrate shell and thus deduce information about the evolution of the shell morphology. This is a unique capability for such opaque systems. We were also able to measure the hydrate growth kinetics (water consumption) consistently using NMR relaxation measurements and observed a transition from heat- to mass-transfer growth control. The initial hydrate shell, following 1 day of growth, was approximately $50\ \mu\text{m}$ thick and, based on the NMR measurement of its surface to volume ratio, was relatively porous. From day 2, consistent data were produced across multiple independent NMR measurements indicating a spherical core with a very low porosity that was shrinking in diameter by approximately $1\ \mu\text{m/day}$.

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Notes

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639 ■ REFERENCES

- 640 (1) Sloan, E. D., Jr.; Koh, C. *Clathrate hydrates of natural gases*, 3rd
641 ed.; CRC press: Boca Raton, FL, USA, 2008.
- 642 (2) Chatti, I.; Delahaye, A.; Fournaison, L.; Petit, J.-P. Benefits and
643 drawbacks of clathrate hydrates: A review of their areas of interest.
644 *Energy Convers. Manage.* **2005**, *46* (9), 1333–1343.
- 645 (3) Hammerschmidt, E. Formation of gas hydrates in natural gas
646 transmission lines. *Ind. Eng. Chem.* **1934**, *26* (8), 851–855.
- 647 (4) Sloan, E. D. A changing hydrate paradigm—From apprehension
648 to avoidance to risk management. *Fluid Phase Equilib.* **2005**, *228*, 67–
649 74.
- 650 (5) Sloan, D.; Koh, C. A.; Sum, A. *Natural gas hydrates in flow*
651 *assurance*; Gulf Professional: Burlington, MA, USA, 2010.
- 652 (6) Turner, D. J. *Clathrate Hydrate Formation in Water-in-Oil*
653 *Dispersions*, Ph.D. Thesis; Chemical Engineering, Colorado School of
654 Mines: Golden, CO, USA, 2006.
- 655 (7) Turner, D. J.; Miller, K. T.; Sloan, E. D. Methane hydrate
656 formation and an inward growing shell model in water-in-oil
657 dispersions. *Chem. Eng. Sci.* **2009**, *64* (18), 3996–4004.
- 658 (8) Sjoblom, J. *Emulsions and Emulsion Stability: Surfactant Science*
659 *Series/61*; CRC Press: Boca Raton, FL, USA, 2012.
- 660 (9) Aman, Z. M.; Olcott, K.; Pfeiffer, K.; Sloan, E. D.; Sum, A. K.;
661 Koh, C. A. Surfactant adsorption and interfacial tension investigations
662 on cyclopentane hydrate. *Langmuir* **2013**, *29* (8), 2676–2682.
- 663 (10) Koh, C. A.; Sloan, E. D.; Sum, A. K.; Wu, D. T. Fundamentals
664 and applications of gas hydrates. *Annu. Rev. Chem. Biomol. Eng.* **2011**,
665 *2*, 237–257.
- 666 (11) Cowie, J.; Bollavaram, P.; Erdogmus, M.; Johnson, T.; Shero, W.
667 *Optimal hydrate management and new challenges in GoM deepwater using*
668 *“Best in Class” technologies*, OTC 17328, presented at the Offshore
669 Technology Conference, Houston, Texas, USA, May, 2–5, 2005;
670 Offshore Technology Conference: Houston, TX, USA, 2005.
- 671 (12) Kelland, M. A. History of the development of low dosage
672 hydrate inhibitors. *Energy Fuels* **2006**, *20* (3), 825–847.
- 673 (13) Ribeiro, C. P., Jr.; Lage, P. L. C. Modelling of hydrate formation
674 kinetics: State-of-the-art and future directions. *Chem. Eng. Sci.* **2008**, *63*
675 (8), 2007–2034.
- 676 (14) Klapproth, A.; Goreshnik, E.; Staykova, D.; Klein, H.; Kuhs, W.
677 F. Structural studies of gas hydrates. *Can. J. Phys.* **2003**, *81* (1–2),
678 503–518.
- 679 (15) Davies, S. R.; Sloan, E. D.; Sum, A. K.; Koh, C. A. In situ studies
680 of the mass transfer mechanism across a methane hydrate film using
681 high-resolution confocal raman spectroscopy. *J. Phys. Chem. C* **2009**,
682 *114* (2), 1173–1180.
- 683 (16) Kerenskaya, G.; Goldschleger, I. U.; Apkarian, V. A.; Janda, K.
684 C. Spectroscopic signatures of halogens in clathrate hydrate cages. 1.
685 Bromine. *J. Phys. Chem. A* **2006**, *110* (51), 13792–13798.
- 686 (17) Luzinova, Y.; Dobbs, G. T.; Raichlin, Y.; Katzir, A.; Mizaikoff, B.
687 Infrared spectroscopic monitoring of surface effects during gas hydrate
688 formation in the presence of detergents. *Chem. Eng. Sci.* **2011**, *66* (22),
689 5497–5503.
- 690 (18) Sloan, E. D., Jr.; Fleyfel, F. A molecular mechanism for gas
691 hydrate nucleation from ice. *AIChE J.* **1991**, *37* (9), 1281–1292.
- 692 (19) Aichele, C. P.; Chapman, W. G.; Rhyne, L. D.; Subramani, H. J.;
693 Montesi, A.; Creek, J. L.; House, W. Nuclear magnetic resonance
694 analysis of methane hydrate formation in water-in-oil emulsions.
695 *Energy Fuels* **2009**, *23* (2), 835–841.
- 696 (20) Packer, K. J.; Rees, C. Pulsed NMR studies of restricted
697 diffusion. I. Droplet size distributions in emulsions. *J. Colloid Interface*
698 *Sci.* **1972**, *40* (2), 206–218.
- 699 (21) Ling, N. N.; Haber, A.; May, E. F.; Fridjonsson, E. O.; Johns, M.
700 L. NMR studies of emulsion microstructure approaching the phase
701 inversion point. *Colloids Surf., A* **2014**, *462*, 244–251.
- 702 (22) Gao, S.; Chapman, W. G.; House, W. Application of low field
703 NMR T₂ measurements to clathrate hydrates. *J. Magn. Reson.* **2009**,
704 *197* (2), 208–212.
- 705 (23) Melnikov, V.; Nesterov, A.; Podenko, L.; Reshetnikov, A.;
706 Shalamov, V. NMR evidence of supercooled water formation during
gas hydrate dissociation below the melting point of ice. *Chem. Eng. Sci.* **2012**, *71*, 573–577.
- (24) Majid, A. A.; Saidian, M.; Prasad, M.; Koh, C., Measurement of
the Water Droplet Size in Water-in-Oil Emulsions Using Low Field
Nuclear Magnetic Resonance for Gas Hydrate Slurry Application. *Can.*
J. Chem. **2015**, DOI: 10.1139/cjc-2014-0608.
- (25) Chen, L.; Sloan, E. D.; Koh, C. A.; Sum, A. K. Methane hydrate
formation and dissociation on suspended gas bubbles in water. *J.*
Chem. Eng. Data **2013**, *59* (4), 1045–1051.
- (26) Taylor, C. J.; Miller, K. T.; Koh, C. A.; Sloan, E. D., Jr.
Macroscopic investigation of hydrate film growth at the hydrocarbon/
water interface. *Chem. Eng. Sci.* **2007**, *62* (23), 6524–6533.
- (27) Makogon, Y.; Mokogon, T.; Holditch, S. *Several aspects of the*
kinetics and morphology of gas hydrates, Proceedings of the Japan
National Oil Conference; 1998; pp 259–267.
- (28) Li, S.-L.; Sun, C.-Y.; Liu, B.; Feng, X.-J.; Li, F.-G.; Chen, L.-T.;
Chen, G.-J. Initial thickness measurements and insights into crystal
growth of methane hydrate film. *AIChE J.* **2013**, *59* (6), 2145–2154.
- (29) Wu, R.; Kozielski, K. A.; Hartley, P. G.; May, E. F.; Boxall, J.;
Maeda, N. Methane–propane mixed gas hydrate film growth on the
surface of water and Luvicap EG solutions. *Energy Fuels* **2013**, *27* (5),
2548–2554.
- (30) Levitt, M. H. *Spin dynamics. Basics of nuclear magnetic resonance*;
John Wiley & Sons: Hoboken, NJ, USA, 2008.
- (31) Traficante, D. D. Relaxation: An introduction. *eMagRes.* **1996**,
DOI: 10.1002/9780470034590.emrstm0452.
- (32) Barrie, P. J. Characterization of porous media using NMR
methods. *Annu. Rep. NMR Spectrosc.* **2000**, *41*, 265–318.
- (33) Kimmich, R.; Anardo, E. Field-cycling NMR relaxometry. *Prog.*
Nucl. Magn. Reson. Spectrosc. **2004**, *44* (3), 257–320.
- (34) Brownstein, K. R.; Tarr, C. E. Spin-lattice relaxation in a system
governed by diffusion. *J. Magn. Reson.* **1977**, *26* (1), 17–24.
- (35) Brownstein, K. R.; Tarr, C. E. Diffusional theory for proton
spin-lattice relaxation in biological cells. *Bull. Am. Phys. Soc.* **1979**, *24*
(3), 346.
- (36) Casanova, F.; Perlo, J.; Blümich, B. *Single-sided NMR*; Springer:
Berlin/Heidelberg, 2011.
- (37) Mitchell, J.; Chandrasekera, T. Understanding generalized
inversions of nuclear magnetic resonance transverse relaxation time in
porous media. *J. Chem. Phys.* **2014**, *141* (22), No. 224201.
- (38) Stejskal, E. O.; Tanner, J. E. Spin Diffusion Measurements: Spin
Echoes in the Presence of a Time-Dependent Field Gradient. *J. Chem.*
Phys. **1965**, *42* (1), 288–292.
- (39) Munday, J. S.; Cotts, R. M. Self-Diffusion Coefficient of Liquid
Lithium. *J. Chem. Phys.* **1968**, *48* (11), 4938–4945.
- (40) Grebenkov, D. S. Laplacian eigenfunctions in NMR. I. A
numerical tool. *Concepts Magn. Reson., Part A* **2008**, *32A* (4), 277–301.
- (41) Lingwood, I. A.; Chandrasekera, T. C.; Kolz, J.; Fridjonsson, E.
O.; Johns, M. L. Emulsion droplet sizing using low-field NMR with
chemical shift resolution and the block gradient pulse method. *J. Magn.*
Reson. **2012**, *214*, 281–288.
- (42) Caprihan, A.; Wang, L. Z.; Fukushima, E. A Multiple-Narrow-
Pulse Approximation for Restricted Diffusion in a Time-Varying Field
Gradient. *J. Magn. Reson., Ser. A* **1996**, *118* (1), 94–102.
- (43) Callaghan, P. T. A Simple Matrix Formalism for Spin Echo
Analysis of Restricted Diffusion under Generalized Gradient Wave-
forms. *J. Magn. Reson.* **1997**, *129* (1), 74–84.
- (44) Ryland, B. N.; Callaghan, P. T. Spin Echo Analysis of Restricted
Diffusion under Generalized Gradient Waveforms for Spherical Pores
with Relaxivity and Interconnections. *Isr. J. Chem.* **2003**, *43* (1–2), 1–
7.
- (45) Barzykin, A. V. Theory of Spin Echo in Restricted Geometries
under a Step-wise Gradient Pulse Sequence. *J. Magn. Reson.* **1999**, *139*
(2), 342–353.
- (46) Grebenkov, D. S. NMR survey of reflected Brownian motion.
Rev. Mod. Phys. **2007**, *79*, 1077–1137.
- (47) Hollingsworth, K. G.; Johns, M. L. Measurement of emulsion
droplet sizes using PFG NMR and regularization methods. *J. Colloid*
Interface Sci. **2003**, *258* (2), 383–389.

- (48) Sloan, E. D., Jr. Fundamental principles and applications of natural gas hydrates. *Nature* **2003**, 426 (6964), 353–363.
- (49) Nakajima, M.; Ohmura, R.; Mori, Y. H. Clathrate hydrate formation from cyclopentane-in-water emulsions. *Ind. Eng. Chem. Res.* **2008**, 47 (22), 8933–8939.
- (50) Nicholas, J. W.; Dieker, L. E.; Sloan, E. D.; Koh, C. A. Assessing the feasibility of hydrate deposition on pipeline walls—Adhesion force measurements of clathrate hydrate particles on carbon steel. *J. Colloid Interface Sci.* **2009**, 331 (2), 322–328.
- (51) Barrer, R.; Edge, A. Gas hydrates containing argon, krypton and xenon: kinetics and energetics of formation and equilibria. *Proc. R. Soc. London, Ser. A* **1967**, 300 (1460), 1–24.
- (52) Wu, R.; Kozielski, K. A.; Hartley, P. G.; May, E. F.; Boxall, J.; Maeda, N. Probability distributions of gas hydrate formation. *AIChE J.* **2013**, 59 (7), 2640–2646.
- (53) Lee, S.; Zhang, J.; Mehta, R.; Woo, T.-K.; Lee, J. W. Methane hydrate equilibrium and formation kinetics in the presence of an anionic surfactant. *J. Phys. Chem. C* **2007**, 111 (12), 4734–4739.
- (54) Sloan, E.; Subramanian, S.; Matthews, P.; Lederhos, J.; Khokhar, A. Quantifying hydrate formation and kinetic inhibition. *Ind. Eng. Chem. Res.* **1998**, 37 (8), 3124–3132.
- (55) Zyliftari, G.; Ahuja, A.; Morris, J. F. Nucleation of cyclopentane hydrate by ice studied by morphology and rheology. *Chem. Eng. Sci.* **2014**, 116, 497–507.
- (56) Vysniauskas, A.; Bishnoi, P. A kinetic study of methane hydrate formation. *Chem. Eng. Sci.* **1983**, 38 (7), 1061–1072.
- (57) Moon, C.; Taylor, P. C.; Rodger, P. M. Molecular dynamics study of gas hydrate formation. *J. Am. Chem. Soc.* **2003**, 125 (16), 4706–4707.
- (58) Karanjikar, P. U.; Lee, J. W.; Morris, J. F. Surfactant effects on hydrate crystallization at the water–oil interface: Hollow-conical crystals. *Cryst. Growth Des.* **2012**, 12 (8), 3817–3824.
- (59) Uchida, T.; Ebinuma, T.; Kawabata, J. i.; Narita, H. Microscopic observations of formation processes of clathrate-hydrate films at an interface between water and carbon dioxide. *J. Cryst. Growth* **1999**, 204 (3), 348–356.
- (60) Mori, Y. H. Estimating the thickness of hydrate films from their lateral growth rates: Application of a simplified heat transfer model. *J. Cryst. Growth* **2001**, 223 (1–2), 206–212.
- (61) Ohmura, R.; Ogawa, M.; Yasuoka, K.; Mori, Y. H. Statistical study of clathrate-hydrate nucleation in a water/hydrochlorofluorocarbon system: Search for the nature of the “memory effect. *J. Phys. Chem. B* **2003**, 107 (22), 5289–5293.
- (62) Genov, G.; Kuhs, W. F.; Staykova, D. K.; Goreschnik, E.; Salamat, A. N. Experimental studies on the formation of porous gas hydrates. *Am. Mineral.* **2004**, 89, 1228–1239.
- (63) Chen, L.; Sloan, E. D.; Koh, C. A.; Sum, A. K. Methane Hydrate Formation and Dissociation on Suspended Gas Bubbles in Water. *J. Chem. Eng. Data* **2013**, 59 (4), 1045–1051.
- (64) Sun, C.-Y.; Chen, G.-J.; Ma, C.-F.; Huang, Q.; Luo, H.; Li, Q.-P. The growth kinetics of hydrate film on the surface of gas bubble suspended in water or aqueous surfactant solution. *J. Cryst. Growth* **2007**, 306 (2), 491–499.
- (65) Rao, I.; Koh, C. A.; Sloan, E. D.; Sum, A. K. Gas Hydrate Deposition on a Cold Surface in Water-Saturated Gas Systems. *Ind. Eng. Chem. Res.* **2013**, 52 (18), 6262–6269.
- (66) Hwang, M.; Wright, D.; Kapur, A.; Holder, G. An experimental study of crystallization and crystal growth of methane hydrates from melting ice. *J. Inclusion Phenom. Mol. Recognit. Chem.* **1990**, 8 (1–2), 103–116.
- (67) Stern, L. A.; Hogenboom, D. L.; Durham, W. B.; Kirby, S. H.; Chou, I.-M. Optical-cell evidence for superheated ice under gas-hydrate-forming conditions. *J. Phys. Chem. B* **1998**, 102 (15), 2627–2632.
- (68) Kini, R. A.; Dec, S. F.; Sloan, E. D., Jr. Methane + propane structure II hydrate formation kinetics. *J. Phys. Chem. A* **2004**, 108 (44), 9550–9556.
- (69) Hirai, S.; Okazaki, K.; Araki, N.; Yazawa, H.; Ito, H.; Hijikata, K. Transport phenomena of liquid CO₂ in pressurized water flow with clathrate-hydrate at the interface. *Energy Convers. Manage.* **1996**, 37 (6), 1073–1078.
- (70) Bruker. <http://www.bruker.com/products/mr/td-nmr/minispec-mq-series/mq-droplet-size-analyzer/overview.html>. 2014.
- (71) Carr, H. Y.; Purcell, E. M. Effects of diffusion on free precession in nuclear magnetic resonance experiments. *Phys. Rev.* **1954**, 94, 630–638.
- (72) Meiboom, S.; Gill, D. Modified spin-echo method for measuring nuclear relaxation times. *Rev. Sci. Instrum.* **1958**, 29 (8), 688–691.
- (73) Fridjonsson, E. O.; Graham, B. F.; Akhfar, M.; May, E. F.; Johns, M. L. Optimized Droplet Sizing of Water-in-Crude Oil Emulsions Using Nuclear Magnetic Resonance. *Energy Fuels* **2014**, 28 (3), 1756–1764.
- (74) Gogolashvili, E.; Dzjubenko, N.; Kuz'mina, N.; Margulis, B. Y.; Martynenko, L. New paramagnetic relaxation reagent for water-in-oil emulsions. *Magn. Reson. Imaging* **1994**, 12 (2), 299–300.
- (75) Caravan, P.; Ellison, J. J.; McMurry, T. J.; Lauffer, R. B. Gadolinium (III) chelates as MRI contrast agents: structure, dynamics, and applications. *Chem. Rev.* **1999**, 99 (9), 2293–2352.
- (76) Brown, J. R.; Seymour, J. D.; Brox, T. I.; Skidmore, M. L.; Wang, C.; Christner, B. C.; Luo, B.-H.; Codd, S. L. Recrystallization inhibition in ice due to ice binding protein activity detected by nuclear magnetic resonance. *Biotechnol. Rep.* **2014**, 3, 60–64.