



# Nucleation curves of methane–propane mixed gas hydrates in the presence of a stainless steel wall



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## ABSTRACT

Nucleation phenomena are important to many applications of gas hydrates and yet the nucleation curves of gas hydrate systems have rarely been measured, presumably due to the experimental difficulties involved. We measured the nucleation curves of Structure II (sII) forming methane–propane mixed gas hydrates in the presence of a stainless steel (SS) wall using the second generation High Pressure Automated Lag Time Apparatus (HP-ALTA MkII). The instrument can apply a large number of linear cooling ramps to a small volume of water under isobaric conditions and record maximum achievable subcooling distributions. The survival curves with respect to methane–propane mixed gas hydrate formation were constructed from the recorded data and then converted to nucleation curves using the novel protocol we had recently reported. The nucleation rates per unit length of the three-phase-line, where the guest gas, water and the stainless steel wall met, were derived as functions of system subcooling. We also extended the measurements of the nucleation curves of the same guest gas hydrate in the presence of a glass wall to lower cooling rates than previously studied, so that the nucleation curves of these two systems could be compared at the same cooling rates. Comparison of the nucleation curves of these two systems showed that the nucleation rates per unit length of the three-phase-line were broadly similar to each other. The same instrument and experimental protocols can be utilized for the derivation of nucleation curves of a guest gas of a different composition and/or in the presence of another solid wall.

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## 1. Introduction

Gas hydrates are ice-like crystalline solids in which typically non-polar guests are enclosed in hydrogen bonded network of water host [1]. Gas hydrates have received considerable research interests because of a wide range of potential applications including gas storage, carbon dioxide sequestration, gas separation and desalination [1,2]. In flow assurance of oil and natural gas pipelines, in contrast, gas hydrates pose risks of blockage of pipelines and associated hazards. As such, prevention of gas hydrate formation is a major goal in the oil and gas industry.

Nucleation phenomena in gas hydrate systems [3–5] are therefore important in many potential applications. The probability of homogeneous nucleation is proportional to the volume of the parent phase in which homogeneous nucleation can take place. Likewise, the probability of heterogeneous nucleation is proportional to the interfacial area at which the heterogeneous nucleation

can take place. For the nucleation probability of ice in pure water, for example, the relevant interfacial area is that between water and the container wall. Thus the most fundamental measure that characterizes the nucleation phenomena is nucleation curves – i.e., the nucleation rates per unit volume of the parent phase for homogeneous nucleation or the nucleation rates per unit area of the interface that is relevant to heterogeneous nucleation – each of which as a function of the system subcooling.

Unfortunately, nucleation curves have hitherto received very little experimental research attention for gas hydrate systems, presumably due to the experimental difficulties involved in such measurements. Gas hydrates are, by definition, multi-component systems which consist of guest gas and host water. The solubility of a typically non-polar guest in water is usually very low, making the rate of mass transfer an important issue. For this reason, gas hydrate can only nucleate at the guest–aqueous interface at which the concentration of the guest in the host is the highest, rendering the area of the guest–aqueous interface the relevant interfacial area for the heterogeneous nucleation of gas hydrates.

It had been recognized that statistical study is necessary for the

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study of nucleation phenomena of gas hydrate systems [6–9]. Because of the typically large heat capacities of high pressure gas systems, most of the past experimental studies adopted the so-called induction time measurements at constant subcoolings for the study of nucleation of gas hydrates. In these studies, either a pressurized system is cooled to a pre-set target temperature or a pre-cooled system is pressurized to a pre-set target guest gas pressure to attain the desired subcooling. Then the induction time – i.e., the time it takes until the onset of nucleation – is typically measured [10]. In theory, the induction time provides the inverse of the nucleation rate of the system at that subcooling. In practice, however, due to the extremely time-consuming nature of the induction time measurements, either the number of the statistics was limited to a small number and/or the longer parts of the induction time measurements had to be cut short by introducing an arbitrary maximum waiting period. Moreover, the size of the interfacial area which is relevant to the heterogeneous nucleation is unique to each system and often unknown. It follows that it is impossible to derive a nucleation curve or the nucleation rate per unit area without the knowledge of the said interfacial area.

We note at this stage that setting a deep target subcooling does not solve the problem; the deeper a target subcooling a greater number of experiments would result in nucleation events prior to reaching the target subcooling, which would preclude the induction time measurements at the target subcooling. Moreover, such an approach is only applicable to deep subcoolings and hence does not contribute to the measurements of the whole nucleation curves which should include nucleation rates at shallow subcoolings.

Another approach is to use water-in-oil (W/O) emulsions with suitable surfactants/co-surfactants. The fraction of water in an emulsion that has formed gas hydrate can be calculated from the heat flow profiles of High-Pressure Differential Scanning Calorimetry (HP-DSC) [11]. A very large number of water droplets dispersed in a continuous oil phase in an emulsion may provide sufficient statistics if secondary nucleation can be avoided. A limitation of this method is that the total oil-water interfacial area in the system is not known, and as such the measured heat profiles cannot be converted to the nucleation rate per unit area of the oil-water interface.

The mass transfer limitations in gas hydrate systems not only defines the interfacial area which is relevant to the heterogeneous nucleation but also renders the stochasticity involved in the nucleation phenomena of gas hydrate systems much larger than that in a single component system such as ice freezing [12–15]. To illustrate the extent of stochasticity involved in nucleation phenomena, and the enormity of the challenges we face, we note that Haymet and coworkers studied the nucleation probability distributions of ice freezing using an Automated Lag Time Apparatus (ALTA) [16,17]. The stochasticity in induction times at constant subcoolings were so great that an arbitrary maximum waiting time of 10000 s had to be set, even with the aid of AgI, a good nucleation agent of ice which is used for cloud seeding [17]. For the 265.57 K data (subcooling of 7.6 K), for example, the minimum induction time observed in that study was less than 200 s, while 11 runs reached the maximum waiting time of 10000 s [17]. It is reasonable to assume that the stochasticity in the induction times at constant subcoolings would have been much greater in the absence of the AgI seeding.

These highly stochastic induction time distributions of ice freezing at constant subcoolings could be effectively compressed by the use of linear cooling ramps which subjected the sample to progressively greater driving force for nucleation until nucleation was forcibly induced. The maximum achievable subcooling distributions obtained in this manner dramatically compressed the stochasticity without a need to introduce any arbitrary cut-off. For

ice, the highly stochastic induction time distributions at constant subcoolings were compressed to only 3–4 K of distribution width in the form of maximum achievable subcooling distributions, even without the aid of AgI [16]. We note, however, this approach can only be adopted for a system that has a small heat capacity.

For gas hydrate systems, a family of High Pressure Automated Lag Time Apparatus (HP-ALTA) enabled measurements of maximum achievable subcooling distributions [12–15,18–24]. Because of the multi-component nature of gas hydrate systems, and the mass transfer issues associated with it, the stochasticity in the maximum achievable subcooling distributions was found to be 20 K–30 K, or an order of magnitude greater than that of the ice system [12–14]. We are yet to be able to convert to, or assess the extent of, the corresponding stochasticity in the induction times at constant subcoolings. Given that the compressed distribution widths of gas hydrate systems in the linear cooling ramp measurements are almost an order of magnitude greater than those in the ice system, the magnitude of the stochasticity in the induction times of gas hydrate systems at constant subcoolings must be astronomically large.

We had in fact attempted to measure such induction time distributions at constant subcoolings using both the first generation HP-ALTA (HP-ALTA Mkl) [23] and the second generation HP-ALTA (HP-ALTA MkII) [19]. It turned out that it could not be done; perhaps not surprisingly, the attempt had to be abandoned in favour of an introduction of an arbitrary maximum cut-off waiting period in such measurements. In short, it does not appear experimentally feasible to measure induction time distributions at constant subcoolings. There is little wonder, then, that characterization of the nucleation curves in gas hydrate systems hitherto remains largely unexplored.

We recently reported a novel protocol to experimentally derive nucleation curves directly from survival curves that can be measured using an HP-ALTA [19]. We then used the newly devised protocol to derive nucleation curves per unit surface area of a quasi-free water droplet that was supported by a chemically inert liquid, perfluorodecalin [19]. We also derived the nucleation curves for a water sample contained in a glass sample cell (aka a ‘boat’) [19]. The comparison of these two data sets at the same cooling rates led to a conclusion that an appropriate measure for the normalization of the nucleation rates in the presence of a solid wall was to the unit length of the three-phase-line where the guest gas, the aqueous phase and the solid wall met, not to the unit area of the aqueous-guest gas interface [19].

This is a novel concept and hence may require more explanation. As we noted above, for gas hydrates of sparingly soluble guests, nucleation is only possible at the aqueous-guest interface where the saturation level of the guest gas is the highest. This high level of guest saturation at the interface precludes the attainment of guest supersaturation that is necessary for nucleation elsewhere [4]. Thus the heterogeneous nucleation probability becomes proportional to the aqueous-guest interfacial area in the absence of a solid wall. When nucleation is induced by a solid wall, however, the heterogeneous nucleation probability is not proportional to any interfacial area. On the one hand, the wetted area of the solid wall that is far away from the guest gas is irrelevant to the heterogeneous nucleation, because the solubility of a guest gas in a solid wall is virtually zero. On the other hand, the presence of the solid wall is not at all accounted for in the size of the water-guest interfacial area. To account for the presence of a solid wall, then, the nucleation probability must be proportional to the length of the three-phase-line (e.g., a narrow stripe-like guest-aqueous area next to the three-phase-line).

Thus the essence of the proposed idea is that the overall heterogeneous nucleation probability in a system will be given by the

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