

Synergistic Effects of Sodium Iodide and Sodium Dodecyl Sulfate at Low Concentrations on Promoting Gas Hydrate Nucleation

Fariba Asadi, Ngoc N. Nguyen,* and Anh V. Nguyen*



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ABSTRACT: Surfactants and/or salts at low concentrations are inherently relevant to gas hydrate formation in nature and industry. However, the combined effects of surfactants and salts at low concentrations on gas hydrate formation are poorly understood. Here, we aim to fill this gap of knowledge by examining the effects of sodium dodecyl sulfate (SDS) and sodium iodide (NaI) at millimolar concentrations on methane hydrate formation. We show that adding NaI to dilute SDS solutions reduces the induction time significantly, promoting gas hydrate nucleation. Meanwhile, adding NaI adversely reduces the growth of methane hydrate. Fundamental studies based on sum frequency generation spectroscopy indicate an electrostatically aligned water layer at the gas–SDS solution interface caused by the charged interface as a result of surface adsorption of dodecyl sulfate anions. This aligned interfacial water layer hinders the nucleation of gas hydrate at the gas–SDS solution interface. Added NaI diminishes the alignment of interfacial water, thereby favoring the nucleation of the gas hydrate. Even though, the adverse (inhibiting) effect of added NaI on the methane hydrate growth remains a puzzling observation that requires further investigations. This study sheds more light on gas hydrate formation in surfactant- and salt-containing systems that are important to many phenomena in nature and applications in the industry.

1. INTRODUCTION

Gas hydrates are crystalline solids composed of water and hydrophobic (nonpolar) gas molecules. Water molecules form an ice-like structure via hydrogen bonding called host structure. Gas molecules (guests) are intensely encaged in the cavities of the host structure and exert a multi-directional force to prevent the host structure from collapsing.^{1,2} A large capacity of storing gases in gas hydrates offers various novel applications, in such areas as separation and storage of gases^{3–11} and sequestration of carbon dioxide.^{12–15} The fully reversible formation of hydrates also provides promising methods for eco-friendly refrigeration^{16,17} and desalination of saline water.^{18,19} However, the formation of gas hydrates in oil/gas pipelines is a well-known hazard to the safety and efficiency of the oil and gas industry because it can lead to blocking of the pipelines.^{20–23} In both situations, the formation of gas hydrates must be controlled in desired manners to realize the opportunities or eliminate the hazards.

A feasible way to achieve these goals is to use additives as promoters or inhibitors for gas hydrate formation.^{24–27} A large number of additives have been reported as either promoters or inhibitors for gas hydrate formation. Especially, surfactants and salts have been intensively investigated because they are directly relevant to gas hydrate formation in nature and the industry. The formation of gas hydrates in nature or pipelines is inevitably affected by natural surfactants and salts. Sodium dodecyl sulfate (SDS) has been widely used as a model surfactant in hydrate research. SDS is well-known for its effective promoting effect on gas hydrate formation. Adding SDS at concentrations above the critical micellization concentration (CMC) increased the rate of ethane hydrate

formation by a factor greater than 700.²⁸ Meanwhile, inorganic salts are well-known hydrate formation inhibitors. Fundamentally, it is believed that surfactant micelles are responsible for increasing hydrate formation kinetics because they facilitate gas dissolution and act as mini gas reservoirs (i.e., storing gas molecules in the interior micellar core) in the solution.²⁸ In contrast, inorganic salts inhibit gas hydrate formation by reducing water reactivity and radically perturbing the tetrahedral network of water.^{29,30} With their strong electrostatic interactions with water molecules, inorganic ions advantageously compete with the dissolved gas molecules for water, therefore, reducing the amount of water available for forming gas hydrates.

However, the formation of gas hydrates in dilute solutions of surfactants and salts is relatively poorly understood. Under low concentration regimes, the effects of surfactants are expected to be different because the micelles are absent. It was found recently that SDS at low (sub-millimolar) concentrations inhibits methane hydrate formation.³¹ Such peculiar inhibition was attributed to an aligned water layer underneath the charged gas–water interface as a result of the interfacial adsorption of ionic surfactants.^{31,32} This electrostatic alignment of interfacial water hinders the nucleation of gas hydrates

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at the gas–water interface because gas hydrate nucleation necessitates a tetrahedral ordering of water molecules.¹ Likewise, sodium halides also behave anomalously under low-concentration regimes. While sodium halides at high concentrations are well-known thermodynamic inhibitors for gas hydrate formation, their solutions at low concentrations (between 50 and 70 mM) were found to act as kinetic promoters.^{33–35}

Nevertheless, to the best of our knowledge, the combined effects of surfactants and salts on gas hydrate formation under low-concentration regimes have never been investigated. Even though, these conditions are inherently relevant to the environments in pipelines or nature, where gas hydrate formation is affected by natural surfactants or inorganic ions (minerals). Oil and gas wells contain mixtures of hydrocarbons, water, and other condensate phases. These mixtures reside in underground formations and contact with various rocks and geological matters before they are extracted out. The water phases dissolve ions from the minerals and rocks. The concentrations of ions in the water phases depend upon the chemistry of the rocks and minerals with which they have been in contact. Previous studies reported considerable concentrations of iodide ions (I^-) in water phases from conventional oil and gas wells.^{36–43} Harkness et al. also indicated a wide range of iodide concentrations in the fluid from shale (unconventional) gases.⁴⁴ Natural surfactants can arise from similar origins. Here, we selected SDS and NaI as models of surfactants and monovalent ions, respectively. Another reason for the selection of NaI for our study is that this salt at low concentrations exhibits a most pronounced effect on gas hydrate formation³⁴ and interfacial water structure^{45–47} relative to other salts. Consequently, any potential effects of the salt on gas hydrate formation and water structure could be monitored. We also complemented our kinetic experiments using sum frequency generation (SFG) vibrational spectroscopy to gain molecular insights into the kinetic observations.

2. EXPERIMENTAL SECTION

2.1. Materials. Chemicals used in this study included SDS (99%, Sigma-Aldrich, St. Louis, MO, U.S.A.), NaI (99.5%, Novachem Pty Ltd), and methane (99.995%, Coregas, Australia). The water used was purified using an Ultrapure Academic Milli-Q system (Millipore, Burlington, MA, U.S.A.).

2.2. Gas Hydrate Formation Experiment. The kinetics of methane hydrate formation were investigated using a typical experimental setup for gas hydrate synthesis (Figure 1). It consisted of a stirred high-pressure cell (Parr Instrument, Moline, IL, U.S.A.), a cooling system (a chiller), and a data acquisition system. The pressure cell was equipped with a pressure transducer, thermocouple (accuracy of ± 0.1 K), gas release valve, and pressure relief valve. During the experiments, the pressure cell was immersed in a bath of water/glycerol mixture (1:1 by weight) whose temperature was maintained at a set point thanks to a chiller (RW-1025G Lab Companion refrigerating bath, Jeitech, Korea). The temperature (T) and pressure (P) inside the cell were simultaneously recorded every 2 s using the National Instruments NI-DAQ 9174 data acquisition device and displayed in both graphic and numerical forms on a computer using Labview VI software. A fuller description of the experimental procedure has been reported elsewhere.³³ We fixed the temperature and pressure to 274 K and 10 MPa, respectively, in reference to the previous studies.^{31,48} These conditions are also in typical ranges widely used in methane hydrate formation experiments.

The rate of gas hydrate formation was calculated on the basis of time-dependent pressure (P) and temperature (T) of gas in the cell following the method described in our previous paper.³⁴ Briefly, gas

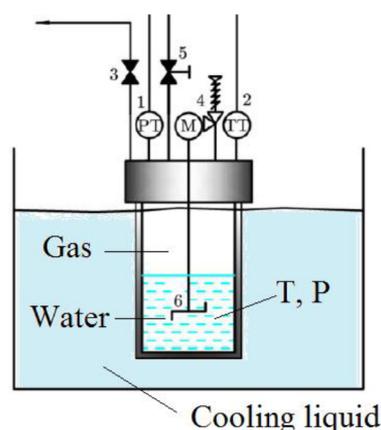


Figure 1. High-pressure cell for methane hydrate formation experiments. Accessory parts include (1) pressure transducer, (2) thermocouple, (3) gas supply valve, (4) safety valve, (5) gas-discharging valve, and (6) stirrer. The temperature and pressure inside the cell were monitored by a computer (not shown).

consumption at time t was calculated using the equation of state of real gas

$$\Delta n(t) = n_0 - n_t = \left(\frac{PV}{ZRT} \right)_{t=0} - \left(\frac{PV}{ZRT} \right)_t \quad (1)$$

where n_0 and n_t are the amounts (moles) of methane at the beginning ($t = 0$) and time t , respectively, R is the universal gas constant, V is the gas volume in the reactor, and Z is the methane compressibility factor and calculated using the Brill–Beggs equation.²⁷ The hydrate growth rate, $r(t)$, was calculated using eq 2

$$r(t) = \frac{d\Delta n}{dt} \approx \frac{\Delta n(t + \Delta t) - \Delta n(t)}{\Delta t} \quad (2)$$

where Δt is the time interval (0.5 min). In practice, we calculated the gas uptake of the hydrate formation based on eq 1. Then, the growth rate of hydrate, $r(t)$, was calculated using the gas uptake versus time (eq 2). We obtained time-dependent growth rate curves against the reaction time. From these curves, we determined the maximum values of the growth rate and used those values to construct Figure 4. Under given operating conditions, the experiments were repeated 5 times to acquire averaged values for the induction time and growth rate.

2.3. SFG Experiment. SFG vibrational spectroscopy measurements were carried out to examine the structural properties of water at the gas–water interface (Figure 2). The details of this method were described in our previous papers.^{31,32} Briefly, the experiments were carried out on a SFG spectrometer (Ekspla, Lithuania), where a

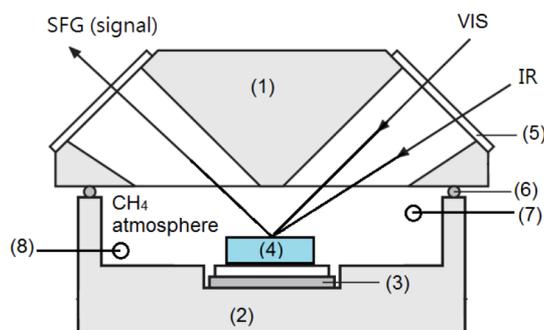


Figure 2. Principle of the SFG probe of the water structure at gas–aqueous interfaces: (1) cell cap, (2) cell base, (3) sample base, (4) solution, (5) transparent CaF_2 crystal windows, (6) O-ring, and (7 and 8) inlet and outlet of methane stream, respectively.

visible (VIS) laser beam and a tunable infrared (IR) laser beam overlapped spatially and temporally on the solution surface (i.e., gas–aqueous interface). The visible beam was generated by frequency doubling the fundamental output pulses (1064 nm and 10 Hz) of 20 ps pulse width from an Ekspla optical parametric generation/amplification and difference frequency system based on LBO and AgGaS₂ crystals. The temperature and relative humidity of the lab were kept constant at 23 ± 2 °C and $66 \pm 2\%$, respectively. The geometry of the SFG setup was the same for all of the measurements with the incident angles of the visible and IR beams equal to 60° and 54°, respectively. All SFG spectra were recorded in a region from 2800 and 3800 cm⁻¹, which is characteristic for the hydrogen bonding of water. The recorded spectra were fitted with a theoretical modulus model of SFG spectroscopy to determine the positions and intensities of relevant peaks. The details of the fitting are presented in our previous publication.³¹

3. RESULTS AND DISCUSSION

3.1. Combined Effects of NaI and SDS on Methane Hydrate Formation. A T – P graph representing the time-dependent temperature and pressure during an experiment is exemplified in Figure 3. A sharp decrease of the temperature at

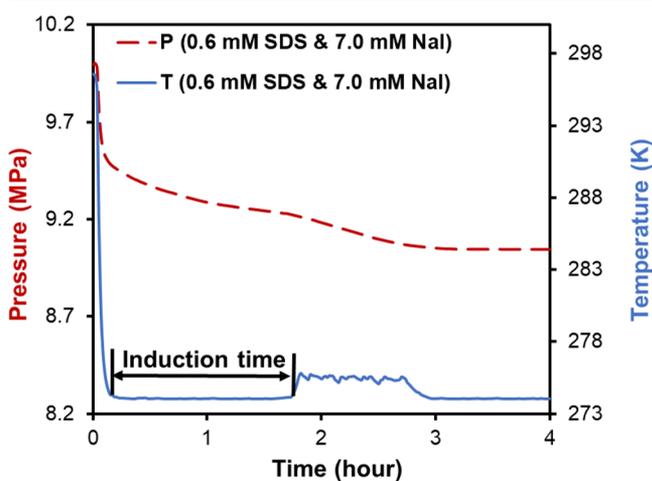


Figure 3. Typical time-dependent temperature and pressure in the methane hydrate formation experiment (P – T graph). An isothermal mode can best describe our experiments. The reactor was kept in a cooling bath having a constant temperature. A fast decrease of the temperature at the beginning was induced by cooling when the reactor was inserted into the cooling bath. The corresponding large drop of the pressure was induced by the gas contraction and dissolution. There was a slight rise of the temperature during exothermic gas hydrate formation.

the beginning was induced by cooling. The corresponding drop of the pressure was induced by the gas contraction and dissolution into the aqueous phase upon cooling. Then, an induction period followed. The temperature remained fairly constant around the set point of 274 K, while the pressure continued to decrease slightly as a result of ongoing dissolution of methane to create a supersaturated solution that was required for the nucleation.^{49–51} The duration of this period is called the induction time. It was followed by a hydrate growth period, which was featured by a sudden rise of the temperature coupling with a steeper drop of pressure. They signify an onset of exothermic formation and growth of methane hydrate inside the cell. The temperature during the growth period was a few degrees (K) higher than the set point because the aqueous phase was constantly heated by the heat of methane hydrate formation. Eventually, both the temperature and pressure approached constant levels, indicating the completion of methane hydrate formation.

The induction time is an important kinetic parameter of gas hydrate formation. As indicated in Figure 3, the hydrate did not form immediately when the system reached the hydrate-forming conditions. Instead, there is a delay (induction period) before the rapid hydrate growth that can be detected experimentally. Dependent upon the chemical nature and the T – P conditions of hydrate systems, the induction time can vary from minutes to hours or days.⁵² The ability to control the induction time is of supreme importance in hydrate practices. In pipelines, a prolonged induction time is needed, so that the transmitted fluids can reach the onshore processing sites before the hydrate formation could occur, therefore, avoiding the formation of hydrate plugs in the pipelines. In contrast, in cases in which the formation of gas hydrates is desired, the induction time has to be reduced by the greatest extent to maximize the productivity of the process.

Only low concentrations are considered in this study because the typical concentration regimes have been widely investigated in the literature.^{24,25} We note that three concentrations of SDS (0.3, 0.6, and 1.0 mM) were considered in reference to the literature.³¹ SDS was found to exhibit an extraordinary inhibition of methane hydrate formation when it was used at concentrations between 0 and 1 mM.³¹ These values are far below the CMC of 8.3 mM for SDS.⁵³ Therefore, any possible effects of surfactant micelles are disregarded in this paper. The concentrations of NaI were also chosen with respect to the literature. Previous findings showed that NaI exhibited a peculiar promotion of gas hydrate formation when

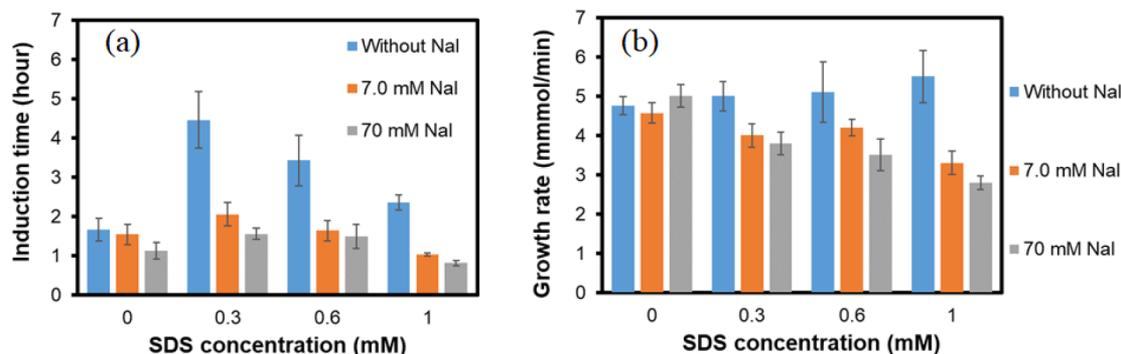


Figure 4. Combined effects of SDS and NaI on the (a) induction time and (b) maximum growth rate of methane hydrate formation. NaI and SDS synergistically reduce the induction time, promoting methane hydrate nucleation. However, they reduce the maximum growth rate of the hydrate.

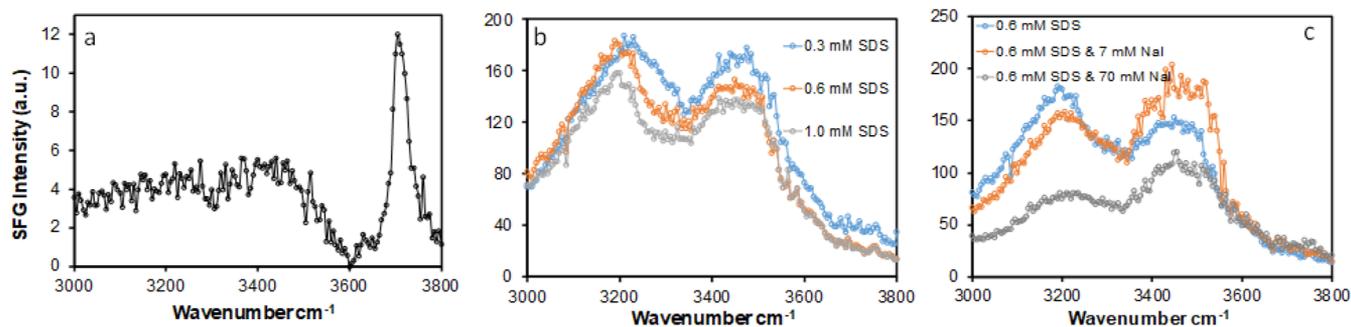


Figure 5. SFG spectra of gas–liquid interfaces in which the liquid phase is (a) pure water, (b) SDS solutions, or (c) mixed SDS/NaI solutions.

it was used at concentrations between 0 and 70 mM. Our special interest is to understand how these two additives collectively affect methane hydrate formation when they are combined, as a situation relevant to reality.

Figure 4a shows the combined effects of SDS and NaI on the induction time of methane hydrate formation. Several important findings are being revealed. First, for pure water, the mean induction time was around 1.7 h. When NaI was added to pure water, the induction time decreased notably. This anomalous promoting behavior of NaI has been reported by a number of studies.^{34,53,55} The promotion was attributed to the hydrophobic-like nature of iodide anion (I^-). The I^- anion and methane molecule have comparable hydration shells.^{56,57} Therefore, the hydration of I^- might serve as seeding the nucleation of methane hydrates.³⁴ More discussions are presented in section 3.3. Second, without NaI (the blue bars), SDS exhibited a significant inhibition of methane hydrate formation when it was used at 0.3 and 0.6 mM. This peculiar inhibiting behavior of SDS has also been observed in our previous work.³¹ We attributed the inhibition to the electrostatically aligned water molecules at gas–water interfaces dictated by the charged surfactants at the interface.³¹ Detailed discussions can be found in section 3.3.

Our particular interest is the combined effects provided by the mixture of SDS and NaI. Figure 4a shows that, for a given SDS concentration, the addition of NaI at the indicated concentrations reduces the induction time by ~50% compared to the cases without NaI. Especially, at the SDS concentration of 1.0 mM, the addition of NaI results in the shortest induction time. Hence, the combined effects of SDS and NaI in the mixture surpass the individual effects exerted by individual SDS and NaI. These results demonstrate an extraordinary synergy between NaI at low concentrations and SDS in promoting methane hydrate nucleation. The mechanism underlying this synergistic effect is discussed in section 3.3.

In addition to the induction time, the growth rate is another important kinetic parameter. Figure 4b shows the combined effects of SDS and NaI on the maximum growth rate of methane hydrate. Surprisingly, the addition of NaI to SDS solutions reduces the maximum growth rate of the hydrate formation. These particular results indicate an apparent inhibiting effect of NaI on the growth of methane hydrate. This is an unexpected observation and contradicts the synergistic effect of NaI on shortening the induction time (Figure 4a). Therefore, the addition of NaI at the investigated concentrations to SDS solutions promotes the nucleation but inhibits the growth of methane hydrate.

3.2. Effect of SDS and NaI on the Water Structure at Gas–Water Interfaces. The nucleation of gas hydrates takes

place favorably at the gas–water interface, where local solubility of the gas is orders of magnitude larger than the solubility in the bulk water.¹ Therefore, the structure of water at the gas–water interface is a vital factor affecting gas hydrate nucleation.^{31,32} Here, we study the structure of interfacial water using SFG spectra. Unlike other vibrational techniques, the SFG is interface-susceptible; therefore, the signals of the bulk phase are eliminated. We note that the SFG instrument cannot operate under high-pressure conditions. Therefore, our SFG results are meaningful for understanding the water structure at the methane–aqueous interface before the onset of gas hydrate formation. In particular, the SFG results are informative to the structure of water at the gas–water interface during the induction period. The behavior of the water structure in this period already determines gas hydrate nucleation.

Figure 5a shows the SFG spectra of the gas–pure water interface. The stretching modes of water molecules are featured by three main peaks. A sharp peak at 3700 cm^{-1} represents the stretching mode of OH groups without a hydrogen bond (also referred to as free OHs or dangling OHs).^{58–60} The two other broad peaks centered at around 3200 and 3450 cm^{-1} reflect the stretching modes of hydrogen-bonded OH groups and, therefore, are informative to the hydrogen-bonded structure of water.^{58–60}

Figure 5b shows the SFG spectra of gas–SDS solution interfaces. There are strict differences between the spectra of SDS solutions and that of pure water. First, the sharp peak characteristic of free OH groups at 3700 cm^{-1} vanishes in the case of SDS solutions. The disappearance of free OHs at charged solution surfaces has been widely reported in the literature.^{31,32,61,62} It infers an electrostatically ordered interfacial water layer underneath the interface that is entirely dictated by an interfacial electrostatic field (IEF) induced by surface adsorption of the negative dodecyl sulfate (DS^-) ions. Meanwhile, the two other peaks at 3200 and 3450 cm^{-1} are substantially enhanced with respect to the case of pure water. The enhancement of these peaks originates from the alignment of molecular dipole moments of water molecules rendered by the IEF underneath the charged interface (as a result of the adsorption of DS^- anions). It was found that the extent of such water alignment correlates with the enhancement of the intensity of the 3200 cm^{-1} peak (denoted as $I_{(3200)}$) relative to the intensity of the 3450 cm^{-1} peak ($I_{(3450)}$).^{31,32,61,62} In other words, the $I_{(3200)}/I_{(3450)}$ ratio reflects the degree of the alignment of water molecules induced by the IEF. Therefore, we use this parameter ($I_{(3200)}/I_{(3450)}$ ratio) to assess the structure of interfacial water at gas–solution interfaces.

Figure 5c shows the SFG spectra of gas–mixed NaI/SDS solution interfaces. Evidently, at a given SDS concentration, i.e., 0.6 mM, the addition of NaI results in a decrease of $I_{(3200)}$ relative to $I_{(3450)}$. As discussed above, the decrease in the $I_{(3200)}/I_{(3450)}$ ratio manifests the moderated alignment of the interfacial water. Therefore, we calculated this ratio for different concentrations of SDS and/or NaI. The results are plotted in Figure 6 from which two important features can be

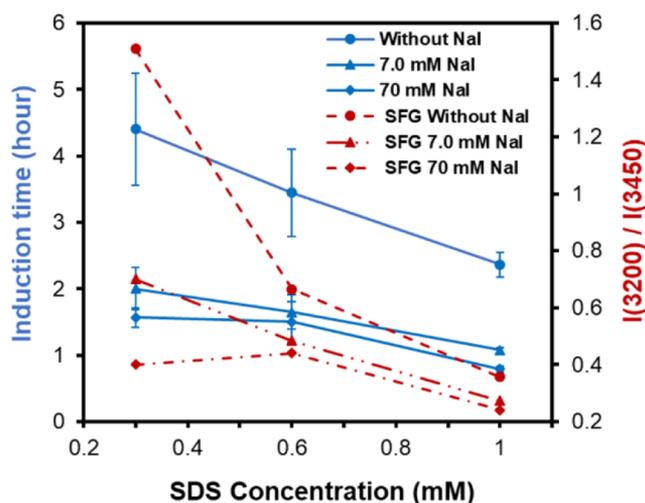


Figure 6. Correlation between the induction time (solid lines) and interfacial water alignment reflected by the $I_{(3200)}/I_{(3450)}$ ratio (dashed lines) at the surface of mixed SDS/NaI solutions. The degree of interfacial water alignment is indicated by the ratio of $I_{(3200)}/I_{(3450)}$ obtained from SFG spectra. Evidently, the addition of NaI to SDS solutions at the investigated concentrations lessens the alignment of interfacial water, thereby promoting the nucleation of methane hydrates.

observed. First, in solutions of SDS without NaI, increasing the concentration of SDS leads to the decrease of the $I_{(3200)}/I_{(3450)}$ ratio. Second, at a given concentration of SDS, adding NaI leads to the decrease of the $I_{(3200)}/I_{(3450)}$ ratio. Interestingly, Figure 6 also shows the correlation between the value of the $I_{(3200)}/I_{(3450)}$ ratio (dashed lines) and the induction time (solid lines). The induction time decreases following a similar decreasing trend of the $I_{(3200)}/I_{(3450)}$ ratio. The physical meaning of this observation is that gas hydrate nucleation is favored when the alignment of interfacial water is reduced. Therefore, it is concluded that the addition of NaI to SDS solutions at the investigated concentrations reduces the degree of water alignment at the gas–SDS solution interface, thereby favoring gas hydrate nucleation.

3.3. General Discussion. We have shown that a mixture of NaI and SDS can accelerate methane hydrate nucleation under certain concentrations; i.e., the concentration of SDS is 1 mM and that of NaI is between 0 and 70 mM (Figures 4a and 6). Therefore, NaI and SDS at these concentrations produce synergistic promoting effects on methane hydrate nucleation. However, the maximum growth rates of methane hydrate were reduced correspondingly (Figure 4b). Therefore, the mixture of NaI and SDS adversely affects the growth of methane hydrate. These apparently contradictory observations can be rationalized by considering the multiple stages of gas hydrate formation. Accordingly, a given additive might act effectively on a certain stage of gas hydrate formation. In some cases, fast

nucleation might result in subsequent slow growth because the ensuing hydrate might act as, for example, a barrier of mass transfer and vice versa. Some kinetic hydrate inhibitors were found to retard the nucleation of gas hydrates within a certain period, but then a rapid growth took place steadily.^{63,64} These particular examples indicate that the effects of additives on gas hydrate formation are complex rather than following straight patterns. The present opposite patterns of NaI/SDS mixtures in affecting the nucleation and growth of methane hydrate provide further evidence of such complexity. In the following, we rationalize these peculiar effects of NaI/SDS.

The increasing promotion of methane hydrate nucleation by adding NaI can be rationalized on the basis of the SFG results. The promotion can be attributed to the reduction of electrostatic alignment of water molecules at the gas–solution interface as a result of the addition of NaI. Accordingly, the interface of the gas–SDS solution is charged by the absorption of DS^- anions, thereby resulting in an IEF. The water molecules in an interfacial layer underneath the interface are aligned, so that their molecular dipole moments tend to be parallel (although they are never perfectly parallel as a result of thermal motions). This aligned configuration of interfacial water is unfavorable for gas hydrate nucleation (which takes place at the gas–water interface) because the nucleation necessitates tetrahedral ordering of water, in which the dipole moments of water molecules have random orientations; therefore, the net molecular dipole moment becomes zero. This phenomenon has been reported and discussed in our previous publications.^{31,32}

Now, we consider the effects of added NaI. Iodide (I^-) is a special and extraordinary ion. It is an inorganic ion but behaves similarly in part to a small hydrophobic molecule, such as methane.^{56,57} As a result of the large radius, I^- has a low charge density. Therefore, the interactions between I^- and surrounding water molecules are weaker than the interactions between water molecules (hydrogen bonding), a situation similar in part to methane–water interactions.^{56,57} This feature gives rise to the hydrophobic-like origin of I^- anions.^{45–47} Hence, the addition of NaI to SDS solutions would lead to two main effects. First, added Na^+ and I^- ions disturb and weaken the IFE created by DS^- surfactants, thereby lessening the degree of water alignment at the interface. This effect of added Na^+ and I^- ions is confirmed by the SFG spectra, as discussed in section 3.2. Second, the I^- anions with their hydrophobic-like nature might have their hydration shells that are structurally similar to the gas hydrate cages, thereby acting as seeding the nucleation of methane hydrate.³⁴ Indeed, the promoting effects of I^- anions at low concentrations on gas hydrate formation have been reported by several studies.^{34,35,54} Such an extraordinary role of I^- has been discussed in our previous publications.^{24,34} These two effects of I^- anions give rise to the promoted methane hydrate nucleation. Meanwhile, the adverse (inhibiting) effect of added NaI on the growth of methane hydrate is a puzzling observation, for which no plausible explanation exists. Possibly, it might be related to kinetic parameters, such as mass transfer. However, further investigations are required for a reasonable explanation.

4. CONCLUSION

We have investigated the combined effects of SDS/NaI mixed solutions at low concentrations on methane hydrate formation. We have shown synergy between NaI and SDS at millimolar concentrations in promoting the nucleation of methane

hydrate. Our SFG studies suggested that added NaI diminished the alignment of water molecules underneath a charged surface of SDS solutions, thereby favoring the nucleation of gas hydrate at the gas–solution interface. However, added NaI was also found to reduce the growth of methane hydrate, which is a puzzling observation. Given the great relevance of mixed salt/surfactant solutions to gas hydrate formation in nature and applied systems, this topic would deserve further research for a fuller and more comprehensive understanding.

AUTHOR INFORMATION

Corresponding Authors

Ngoc N. Nguyen – School of Chemical Engineering, The University of Queensland, Brisbane, Queensland 4072, Australia; Physics at Interfaces, Max Planck Institute for Polymer Research, 55128 Mainz, Germany; orcid.org/0000-0002-0999-1176; Email: nguyenn@mpip-mainz.mpg.de

Anh V. Nguyen – School of Chemical Engineering, The University of Queensland, Brisbane, Queensland 4072, Australia; orcid.org/0000-0001-6703-2291; Email: anh.nguyen@eng.uq.edu.au

Author

Fariba Asadi – School of Chemical Engineering, The University of Queensland, Brisbane, Queensland 4072, Australia

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acs.energyfuels.0c01725>

Notes

The authors declare no competing financial interest.

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