Unexpected inhibition of CO₂ gas hydrate formation in dilute TBAB solutions and the critical role of interfacial water structure

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Abstract

Gas hydrates formed under moderated conditions open up novel approaches to tackling issues related to energy supply, gas separation, and CO₂ sequestration. Several additives such as tetra-n-butylammonium bromide (TBAB) have been empirically developed and used to promote gas hydrate formation. Here we report unexpected experimental results which show that TBAB inhibits CO₂ gas hydrate formation when used at minuscule concentration. We also used spectroscopic techniques and molecular dynamics simulation to gain further insights and explain the experimental results. They have revealed the critical role of water alignment at the gas-water interface induced by surface adsorption of tetra-n-butylammonium cation (TBA⁺) which gives rise to the unexpected inhibition of dilute TBAB solution. The water perturbation by TBA⁺ in the bulk is attributed to the promotion effect of high TBAB concentration on gas hydrate formation. We explain our finding using the concept of activation energy of gas hydrate formation. Our results provide a step toward to mastering the control of gas hydrate formation.

Keywords: TBAB, gas hydrate, CO₂, water structure, SFG, FTIR, MD

1 Introduction

Gas hydrates have been a topic of tremendous interest owing to their fascinating science and enormous potential for applications. They are ice-like crystalline solids comprising water and a suitable gas [1]. The water molecules (the host molecules) form a cage-like structure encaging the gas molecules (the guest molecules) inside; and the encaged gas molecules, in turn, stabilize the cage-like structure by creating a multidirectional repulsive force, preventing the whole caging structure from collapsing [1, 2]. Such cooperative interaction allows gas hydrates to form at temperatures well above the freezing point of pure (clean or neat) water.

Despite the astounding simplicity of their chemical compositions, the scientific picture behind gas hydrates phenomena is extraordinary and fascinating. Moreover, the immense potential of gas hydrates-related applications has further drawn the attention of researchers towards this field. However, to utilize gas hydrates, one typically needs to use additives to control the kinetics of hydrate formation. The additives can be either inhibitors or promoters whose influence is either to slow down or to foster the evolution of gas hydrates, respectively. While hydrate inhibitors have attracted the remarkable attention of researchers since gas hydrates were found to cause flow plugging of submarine gas/oil pipelines [3-5], gas hydrate promoters are an emerging research area. Very active activities of recent studies have aimed at developing well-performing promoters for novel approaches to gas storage and transportation [5-7], gas separation [8-15] and sequestration of anthropogenic carbon dioxide [16-19] via a mean of gas hydrates.

Of the possible promoters, tetra-n-butylammonium bromide has received the considerable attention of researchers owing to its high effectiveness. However, previous works primarily focused on the influence of TBAB of high concentration. For this range of concentration, TBAB has been consistently reported as an effective promoter [8, 9, 12, 14]. Moreover, the science underlying the promoting mechanism of gas hydrate formation in such solutions of TBAB has not been well understood. The conventional way to explain the promoting behavior of TBAB is to assume that TBAB forms its clathrate first and then TBAB clathrate functions as the seeding of gas hydrate formation. However, how this phenomenon can be understood at molecular scale would require more powerful techniques both experimentally and computationally. In this work, we examined the influence of TBAB of a wide range of concentration, from several mM to several M, on the formation of CO₂ gas hydrates. We observed an unexpected inhibition effect of

TBAB at an extremely low concentration (around 0.125% by wt. or 3.8 mM), contrasting to the well-known promotion behavior of concentrated TBAB solutions. This inhibition effect of TBAB is extraordinary and, therefore, is of fundamental importance. Specifically, we employed Sum Frequency Generation (SFG) vibrational spectroscopy and Attenuated Total Reflection Fourier Transform Infrared spectroscopy (ATR-FTIR) to study the molecular mechanisms underpinning our observation. In addition, we also utilized molecular dynamics (MD) simulation to qualify our spectral interpretation. The synergic combination of spectral and computational results signifies the interplay of water orderliness in governing gas hydrate formation and provides significant insights into the mechanism of gas hydrate promotion and inhibition. The outcome of this work could be a step toward advancing the use of additives to control gas hydrate formation.

2 Materials and Experimental Methods

2.1 Materials

Chemicals used in this study included carbon dioxide (98.3%, Coregas, Australia) and tetra-n-butylammonium bromide (98%, Wako, Japan). Deionized water used in this work was produced by a Milli-Q purification system (Millipore, USA) with a resistivity of 18.2 M Ω .cm.

2.2 Experimental Methods

Gas hydrate kinetics experiments were carried out using a typical experimental setup for gas hydrate synthesis, which consists of a high pressure reactor (Parr Instruments, USA), a cooling system and gas supply system. The instantaneous temperature and pressure inside the reactor were simultaneously monitored and recorded by a data acquisition system. The time-dependent gas uptake and growth rate of gas hydrates were calculated using state equation of real gas, and the compressibility factor of gaseous CO₂ was calculated using Pitzer's correlations [20]. A fuller description of the experimental procedure and calculation method has been reported in our previous publications [21, 22].

Sum Frequency Generation (SFG) vibrational spectroscopy measurements were carried out on EKSPLA SFG system (EKSPLA, Lithuania). The visible beam and the tunable IR beam were overlapped spatially and temporally on the solution interface. The visible beam was generated by frequency doubling the fundamental output pulses (1064 nm, 10 Hz) of 20 ps pulse-

width from an EKSPLA solid state Nd:YAG laser. The tunable IR beam was generated from an EKSPLA optical parametric generation/amplification and difference frequency system based on LBO and AgGaS₂ crystals. The tunable IR beam energy only fluctuated with a standard deviation of 3.0%, while that of the visible beam was 1.5%. SFG measurements were carried out using ssp polarization combination of the output and input beams (s-polarized SFG, s-polarized visible and p-polarized IR) with the incident angle of the visible beam set to $\alpha_{vis} = 60^\circ$ and that of the IR set to $\alpha_{IR} = 54^\circ$. The signal was fine-tuned at 2900 cm⁻¹ for 2750-3000 spectral region and at 3200 cm⁻¹ for 3000-3800 region. SFG signals reported in this paper were normalized by dividing the measured values by the IR and visible intensities.

Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) spectroscopy: ATR-FTIR spectra of the TBAB solutions were recorded on a Nicolet iS50 FTIR bench equipped with an iS50 single bounce diamond ATR module (Thermo Scientific, Madison, USA) by co-adding 64 scans at 4 cm⁻¹ spectral resolution. A spectrum of pure water was scaled and subtracted from each TBAB solution, adjusting the scaling factor to achieve a null in the total integrated intensity of the OH stretching band of water. Spectral manipulations were performed with the Nicolet Omnic 9.0 software (Thermo Scientific, Madison, USA).

Molecular dynamic simulation: The molecular models were built by using AmberTools14 and molecular dynamics simulations were carried out using Amber9 software [23, 24]. We used TIP4P-ew for water model [25]. TBAB molecule was modeled using the all-atoms carbon model with hydrogen atoms being explicitly described [26]. The molecular parameters (bonds, angles, and torsions) were retrieved from General Amber Force Field (GAFF) and literature [27, 28]. Once all individual molecules had been created, they were then packed into simulation box using Packmol package [29]. Simulation box is orthogonal with x , y and z dimensions being 50, 50 and 100 Å, respectively. The box is divided into three spatial zones on z -axis, of which aqueous solution of TBAB occupied $15 \text{ Å} \leq z \leq 85 \text{ Å}$ zone and gas occupied the rest of the box. This configuration means that there were two gas/solution interfaces positioning at $z_{low} = 15 \text{ Å}$ and $z_{high} = 85 \text{ Å}$, respectively. The number of TBAB molecules in simulation boxes was 10, 15 and 30 while the number of water molecules varied accordingly, resulting in total concentration of TBAB equivalent to 0.095, 0.142 and 0.285 M, respectively. These systems are called System A, B and C, respectively.

For each simulation, after running energy minimization, molecular dynamics was performed for 40 (ns) with the time increment of 2fs which is equivalent to a total of 2×10^7 time steps. Simulations were run with NPT ensemble with temperature coupling controlled using the Langevin dynamics scheme and pressure scaling controlled using the Berendsen barostat, and the long-range cutoff radius was 11 Å. SHAKE algorithm was used to control bond length constraint. The simulation outputs were written out after every 10^4 steps.

In our calculation, the interfacial concentration was defined as the number of TBA^+ adsorbed onto gas/water interface divided by interface area (mol/m^2 , also known as surface excess). Bulk concentration was defined as the number of TBA^+ cations divided by the volume of bulk phase. And, the total concentration is the number of total TBAB molecules put in simulation box divided by the volume of the aqueous zone. The details of calculation are presented in Supporting Information. Simulations were carried out using computational resources provided by Pacific Northwest National Laboratory.

3 Results and Discussion

3.1 Unexpected inhibition of hydrate formation in dilute TBAB solutions

Figure 1 shows typical changes in the instantaneous pressure (P) and temperature (T) versus time for CO_2 gas hydration formation, as recorded directly from the hydrate formation reactor. A brief description of what happened is as follows. When the pressure reached the desired value of 2.65 MPa, the gas supply was terminated by disconnecting the reactor from gas cylinder. Consequently, the pressure started to drop for the first time, mainly due to the dissolution of CO_2 in water. At the same time, the temperature increased swiftly from initial value of around 1.5°C to about 3°C as a result of the system being warmed up by sensible heat of the feed gas as well as latent heat of CO_2 gas dissolution. Within the next 10 minutes, the pressure remained constant while the temperature decreased to around the initial value, indicating that the dissolution of CO_2 in water was completed. Then, the pressure started to drop substantially for the second time while the temperature increased suddenly. The 2nd decrease in pressure was caused by the uptake of gas by gas hydrate formation while the 2nd increase of the temperature was induced by the exothermal formation of gas hydrate, which both clearly indicate the onset of gas hydrate formation inside the reactor. Eventually, the pressure approached

constant (equilibrium) level while the temperature fluctuated around the initial value, showing that the formation of CO₂ gas hydrate was approaching the completion.

Figure 1. Typical changes in the instantaneous pressure (P) and temperature (T) versus time for CO₂ gas hydrate formation. The concentration used was 3%TBAB (by weight). The second drop in P and the rise in T provide a strong evidence and a significant signal of the exothermal formation of CO₂ gas hydrate.

Figure 2 shows the experimental results for CO₂ uptake versus TBAB concentration and time. The gas uptake increases with time as expected. The dependence of the gas uptake on TBAB concentration is interesting and surprising. With increasing TBAB concentration from zero (pure water), the gas uptake decreases first, going through a minimum and then increases to a maximum level of high concentration. The gas uptake at high TBAB concentration is well reported in the literature and is assigned to the promotion of gas hydrate formation by TBAB [8, 9, 12]. The minimum gas uptake at a concentration of around 0.125% (by wt.) is lower than that of pure water. For example, the gas uptake after 300 minutes by 0.125% TBAB solution is 0.026 (mol/mol water), equivalent to a reduction of 40% in comparison with that of pure water (0.044 mol/mol water). In contrast, 1% TBAB solution could enhance gas consumption by 14%, from 0.044 (mol/mol water) to 0.050 (mol/mol water). Evidently, at the dilute concentration of 0.125% TBAB displays an inhibition effect on the gas uptake which has not been reported previously and is unexpected. The dual effect of TBAB on inhibiting and enhancing gas uptake at low and high concentrations, respectively, is similar to the dual effect of NaX ($X = \text{I}, \text{Cl}$) on gas hydrate formation, which was observed and reported from our laboratory previously [21, 30].

Figure 2. Experimental results for gas uptake versus TBAB concentration and time: The dual effect of TBAB on the formation of CO₂ gas hydrates. There is a region of gas uptake lower than that of pure water at a concentration of around 0.125% by wt. This unexpected inhibition of CO₂ gas hydrate formation by TBAB has not been reported previously. The red area indicates a significant enhancement in gas uptake in higher concentration range. Experiments were carried out under an isochoric condition with the temperature set to 1.5°C and initial pressure of 2.65 MPa.

The growth rate of gas hydrate could be calculated using the measured gas uptake shown in Figure 2. The results for the growth rate are shown in Figure 3. The details about the method of calculation are described in our previous publication [21]. Similar to the gas uptake, the growth rate of gas hydrate also underwent the same dual pattern of TBAB concentration dependence (Figure 3). The rapid growth rate was observed with solutions of high TBAB concentration (e.g. 1 and 3%) while the growth rate in dilute TBAB solutions (e.g. 0.075 and 0.125%) was slow. The rate of CO₂ gas hydrate growing in pure water at a short time (< 60 min) was between the two growth rates. At a long time, the growth rate in pure water became higher than the growth rate of hydrates in TBAB solutions of high TBAB concentrations because hydrate formation in concentrated TBAB solution was approaching completion. It is noted that for clarity and readability only four of the investigated concentrations of TBAB (excluding pure water) are selectively shown on Figure 3 since the other concentrations show the similar trend.

Although the promoting effect of TBAB on gas hydrate formation is widely reported in the literature [8, 9, 12], the inhibiting effect is extraordinary which would be significant both scientifically and practically. Scientifically, the dual effect can challenge our current understanding of the molecular mechanism governing gas hydrate promotion and inhibition which is discussed further in the following sections. Practically, the dual effect requires careful control of TBAB concentration used in the industry, which can have either inhibiting effect or promoting effect on gas hydrate formation at low or high concentration, respectively.

Figure 3. The rate of CO₂ gas hydrate growth in TBAB solutions versus time and TBAB concentrations. At the short time, the growth rate of hydrates in pure water is higher than the growth rate in dilute TBAB solutions but lower than the growth rate in solutions of high TBAB concentrations. The dual effect of TBAB on the formation of CO₂ gas hydrates is also confirmed by their growth rate.

3.2 The effect of TBAB on water structure

SFG and ATR-FTIR spectroscopic techniques were employed to examine water structure at the interface and in the bulk solution, respectively, to explain the experimental observation reported in the previous section. SFG spectroscopy is inherently surface-specific and, therefore, is suitable for probing water structure at interfaces [31-36] while in ATR-FTIR technique, the incident beams can penetrate in to bulk phase (through a depth of 1 μm) to signify the structural property of the bulk [37]. Hence, SFG and ATR-FTIR provide an excellent combined tool to gain a full picture of changes in water structure [36] and correlate them with the experimental results. In particular, we focused on the changes in water structure of low and high TBAB concentration solutions.

3.2.1 Dual effect of TBAB on the interfacial water structure

The left panel of Figure 4 shows the measured SFG spectra of the interfacial water of TBAB solutions of different concentrations. TBAB have a strong dual effect on the structure of interfacial water molecules as evidenced by the change in the magnitude of the strongly hydrogen-bonded (ice-like) OH peak at 3200 cm^{-1} . With increasing TBAB concentration from 0% (pure water), the peak intensity first increases rapidly, reaching a maximum at TBAB concentration of about 0.125%, and then slowly decreases back to the spectrum of pure water at high TBAB concentration. The right panel of Figure 4 shows the peak intensity versus TBAB concentration. Evidently, this change in interfacial water structure is very similar to the change in the gas uptake presented in Section 3.1.

Figure 4. SFG spectra of the surface of TBAB solution of various concentrations (left), and the height of the peak at 3200 cm^{-1} as a function of TBAB concentration (right). The substantial increase in the water signal at low TBAB concentrations manifests the increasing orderliness of surface water structure of dilute TBAB solutions. The decrease in the SFG amplitude signal at high TBAB concentration shows that water became less ordered at the surface of concentrated solution compared to that of dilute TBAB solutions.

3.2.2 Effect of TBAB on the bulk water structure

Figure 5 shows the measured ATR-FTIR spectra of TBAB solutions. The water background was subtracted from these spectra. There are three sharp positive peaks centering at 2880 , 2940 and 2975 cm^{-1} , followed by a broad negative (weaker than water) peak at around

3200 cm^{-1} and one broad positive (stronger than water) peak at around 3400 cm^{-1} . The first three peaks present the stretching modes of alkyl group [33, 35, 38]. Their intensities were found to be proportional to TBAB concentration in the solutions (see the Supporting Information). This feature of alkyl regime confirms the reliability and bulk-specificity of the ATR-FTIR spectra. The two broad peaks at 3200 cm^{-1} and 3400 cm^{-1} present the characteristic stretches of hydrogen-bonded OH of bulk water. They are significant to the findings described in the previous section.

Figure 5. Experimental results for the absorbance of ATR-FTIR signal of TBAB solutions. The signals were offset for the background by subtracting the water signal (measured separately) using the built-in software of the ATR-FTIR device. If the measured signal was weaker than that of water, the shown absorbance is below the zero water line (negative). TBAB strengthened the peak at 3400 cm^{-1} for weakly hydrogen-bonded (liquid-like) OH in the solutions and weakened the peak at 3200 cm^{-1} for strongly hydrogen-bonded (ice-like) OH.

As can be seen from Figure 5, the magnitudes of these two peaks are significantly influenced by TBAB concentration. The peak of the weakly hydrogen-bonded OH at 3400 cm^{-1} was proportional to the TBAB concentrations. At low TBAB concentrations (0-0.5%), the increase in the 3400 cm^{-1} peak was incremental. In particular, there is no significant difference among the peak heights at 0.075, 0.125 and 0.5% of TBAB. At high TBAB concentration ($>0.5\%$), the increase in the 3400 cm^{-1} peak was rapid, and peak heights are proportional to TBAB concentration. For example, the peak height at 1% TBAB is almost double of the peak height at 0.5% TBAB and the peak height at 3% TBAB is almost triple of the peak height at 1% TBAB.

On the contrary to the weakly hydrogen-bonded OH at 3400 cm^{-1} , the off-set absorbance of the strongly hydrogen-bonded OH at 3200 cm^{-1} is negative as shown in Figure 5. It is an evidence of the weakening of the ATR-FTIR signal of the strongly hydrogen-bonded OH at 3200 cm^{-1} by TBAB. Interestingly, the ATR-FTIR signal was first decreased by increasing TBAB from 0 (pure water) to about 0.075% concentration and then was increased back to that of water at about 0.125% concentration. At TBAB concentrations higher than 0.125%, the height of the 3200 cm^{-1} peak rapidly decreased with increasing TBAB concentration. The offset peak value at 3% TBAB was smaller than the peak value at 1% TBAB by a factor of about 1/4.

Our experimental ATR-FTIR results showing the increase in the 3400 cm^{-1} peak for weakly hydrogen-bonded OH and the decrease in the 3200 cm^{-1} peak for strongly hydrogen-bonded OH provide a solid evidence of the significant effect of TBAB on weakening the hydrogen bond network of the bulk water. These ATR-FTIR results help explain the experimental observation presented in Section 3.1 as to be discussed shortly in Section 3.4.

3.3 Results of molecular dynamic simulation

The typical MD results for interfacial and bulk TBAB ions are shown in Figure 6 for three cases of low, intermediate and high (total) concentrations of TBAB molecules inserted randomly into the simulation box at the beginning of the simulation. The local concentrations of TBA^+ at the interfaces (C_i , also known as surface excess) and in the bulk (C_b) of simulation boxes were computed for the total concentration (C_t) of TBAB packed into the box initially. The insets (a), (b) and (c) respectively show the snapshots of simulation boxes of systems A, B and C after 40 ns to exemplify the numerical data. For $C_t = 0.095\text{ M}$ (System A), the results show $C_i = 0.33$

$\mu\text{mol}/\text{m}^2$ and negligible concentration of TBAB remaining in the bulk solution, $C_b = 0$ M. However, when C_t increases to 0.142 M (System B), C_i increases to $0.40 \mu\text{mol}/\text{m}^2$ but C_b increases suddenly from 0 M to 0.033 M (or 1% wt.). Further increase in C_t to 0.285 M (System C), C_i continues to increase to $0.73 \mu\text{mol}/\text{m}^2$ whereas C_b grows up rapidly to 0.100 M (or 3.5% wt.). Although experimental data of surface excess of TBA^+ is not available, our computed surface excess is comparable with that of common surfactants like tetradecyl trimethyl ammonium bromide ($0.8 - 1.6 \mu\text{mol}/\text{m}^2$ [39]) or sodium dodecyl sulfate ($0.1 - 5 \mu\text{mol}/\text{m}^2$ [40]).

Figure 6. Typical results of molecular dynamics simulation for interfacial, bulk and total concentrations of TBAB obtained for three cases of low, intermediate and high TBAB concentration. The bar charts for Systems A, B and C show the concentration of TBA^+ cations at interfaces and in the bulk of simulation boxes versus the overall concentration of TBAB. The insets (a), (b) and (c) show, respectively, the snapshots of simulation boxes of System A, B, and C. On the snapshots, dark blue symbol shows the TBA^+ ions, bronze symbol the Br^- ion and line the water molecules. The gas phase is hidden for clarity. Evidently, in dilute TBAB solutions, TBA^+ cations are located at the gas-solution interfaces while when at high concentrations, the cations are also present in the bulk phase. The numbers in the figure are shown with different units for the interfacial TBAB concentration, TBAB concentration in the bulk solution and (total) concentration of the TBAB molecules inserted randomly into the simulation box at the beginning.

Evidently, TBAB surfactant is strongly surface-active. The (interfacial) concentration of TBA^+ cations at the air-water interface increases with increasing the total TBAB concentration. In our simulation (see Method), the ions of TBAB and water were initially packed randomly in the aqueous zone $15 \text{ \AA} \leq z \leq 85 \text{ \AA}$. With increasing the simulation running time, TBA^+ cations undergo thermal motion and move to the interfaces where they are retained (adsorbed) to minimize their free energy, resulting in an enrichment of TBA^+ at the interfaces. Experimentally, the presence of TBA^+ cations at solution surface is qualitatively shown by the occurrence of alkyl vibration modes on SFG spectra (see Supporting Information).

Our MD simulation results quantitatively show a significant effect of total TBAB concentration on TBA^+ concentration at the solution surface and in the bulk solution. Importantly, our simulation findings agree well with and reinforce the interpretations of the measured SFG and ATR-FTIR spectra. Firstly, it is shown that the bulk residing concentration of TBA^+ of System A is 0 M. In this case, all of TBA^+ cations adsorb onto the gas-solution interface, as illustrated by inset (a) in Figure 6 (It is noted that in reality the bulk concentration, C_b , is not equal to zero. The calculated $C_b = 0$ here means that the bulk concentration is too low for finding a TBA^+ cation within a given solution volume equivalent to the volume of aqueous phase of simulation box). Secondly, when interfacial concentration of TBA^+ reaches $0.4 \mu\text{mol/m}^2$, the bulk residing TBA^+ concentration increases suddenly to 0.033 M. Then, the bulk concentration continues to increase with the interfacial concentration. This calculated data confirms that in very dilute TBAB solutions, most of TBA^+ cations reside at the solution interface whereas the cations start packing massively in the bulk solutions when TBAB concentration is high, as shown by insets (b) and (c) in Figure 6. Experimentally, these simulation cases correspond to the experiments of gas hydrates, SFG and ATR-FTIR spectroscopies at minuscule and high concentrations of TBAB added to the bulk solutions. Under the condition of low total TBAB concentration, the majority of the added TBA^+ cations prefer adsorbing onto the interface, and an only vanishingly small portion of the cations remains in the bulk solution. Hence, the rapid change in the interfacial water structure into the order state at the 3200 cm^{-1} peak is significant as revealed by the SFG experiments, but the change in the bulk water is not strong as shown by the ATR-FTIR experiments. The consequence of adding a minuscule TBAB amount into water is the unexpected inhibition of gas hydrate formation as experimentally probed.

When the added TBAB concentration is high, the concentration of TBA^+ cations residing in the bulk solution is increased as per the MD simulation results. It leads to the weakening of hydrogen bond network in the bulk as evidenced by the ATR-FTIR results shown in Figure 5. The weakening of the bulk hydrogen bond network is responsible for the promotion of gas hydrate formation as revealed by the gas uptake experiments.

3.4 General discussion

Our computational and experimental (SFG and ATR-FTIR) results are very informative to water structure. Spectroscopically, the vibration of water molecules is affected by surrounding environment, in which strongly and weakly hydrogen-bonded OHs vibrate at lower and higher frequencies, respectively [41]. Indeed, it is known that the spectral band at 3200 cm^{-1} arises from strongly hydrogen-bonded water and explicitly manifests the ordered state of water while the band at 3400 cm^{-1} arises from weakly hydrogen-bonded water and, therefore, it manifests disordered water with a lesser degree of hydrogen bond [42-44]. Therefore, spectral increase at 3200 cm^{-1} provides direct evidence of the strengthening of both water structure and hydrogen bonds and vice versa. Likewise, spectral increase (decrease) at 3400 cm^{-1} indicates a weakened (strengthened) water structure owing to a decrease (increase) in the ordering of hydrogen bonds [35, 44, 45]. This spectral information about water structure is helpful in understanding the effect of TBAB on inhibiting and promoting gas hydrate formation as discussed below.

Our results show the significant changes in gas hydrate kinetics and both interfacial and bulk water structures as a function of TBAB concentration. In low concentration regime, TBAB shows no discernible effect on water structure in the bulk, but significant reduction in hydrate kinetics and strong water alignment at the interface are evident (both at 0.125% TBAB). Therefore, the water alignment at the gas-water interface is responsible for gas hydrate inhibition. This aspect of the unexpected gas hydrate inhibition and its link to water alignment at the gas-water interface has not been reported previously. This observation also implies an important role of interfacial water in governing gas hydrate formation. Indeed, gas hydrate formation starts at the interfaces [46], which are the locations of direct gas-water contact being of paramount importance for gas hydrate nucleation [1]. It is worth noting that gas hydrate formation is a successive transformation of water structure from a liquid state into the clathrate-like solid state [1, 8, 47]. In this process, water molecules have to rearrange themselves to

accommodate the gas molecules. As the nucleation takes place at the gas-water interfaces [1, 46], the local water needing to rearrange themselves are those water at interfaces. Thus, initially strong hydrogen-bonded (aligned) water at the interfaces in the presence of TBAB of very low concentration becomes unfavorable for the rearrangement. Otherwise, it would require a higher driving force to surpass the interaction between water dipoles and external electrostatic field (This field is induced by charged interface due to surface adsorption of TBA^+). Consequently, the nucleation of gas hydrate is inhibited.

In contrast, in high concentration regime, water is radically perturbed by TBA^+ cations (both at the interface and in the bulk). Also, most of TBA^+ cations reside in the bulk and become hydrophobic solute. Water cluster around TBA^+ is disordered as seen through a spectral shift to higher stretching frequency on the ATR-FTIR spectra. A similar weakening of water structure around some other hydrophobic solutes is discussed in the literature [48, 49]. Consequently, the local water structure around TBA^+ cations would become more dynamic and energetic, and tends to transform into a more ordered conformation which is the semi-clathrate hydrate of TBA^+ . Then, TBA^+ semi-clathrate seeds the nucleation of CO_2 gas hydrate. Therefore, TBAB used with a high concentration becomes a promoter of gas hydrate formation.

It is noted that the literature related to gas hydrates has been increasing exponentially and a huge number of possible additive compounds have been intensively investigated [50]. However, previous works usually targeted the research at macroscopic measurements of kinetics rather than paying the attention to the induced change in water structure. Macroscopic measurements of kinetics usually produce experiment-specific results, meaning that the experimental observations depend on experimental conditions adopted (e.g. types and concentrations of additives, types of gases, types of equipment, etc.), so the results are difficult to be generalized [50]. To gain a universal understanding of the effect of additives, we must be able to understand how water structure, as the direct involvement in gas hydrate formation, is changed accordingly. The ability of perceiving the change in water structure can provide a key guiding scientists in designing the new forms of additives (either new molecular structures or mixing the available compounds) to control the formation of gas hydrates at molecular scale. Our current work has shed light into this new direction, and would be a step towards the universal understanding of the influence of additives on gas hydrate promotion and inhibition. Another point worth discussing is the fact that, in addition to CO_2 , methane (CH_4) is also a popular hydrate former and both of these gases

form structure I of gas hydrates [5]. But CO_2 is different from CH_4 in that it is more polar and slightly dissociates in water (CH_4 is absolutely chemically inert to water under the condition of gas hydrate experiments). As previously discussed, the way we addressed the inhibition (or promotion) of gas hydrate is based on the induced change in water structure and, thus, providing a universal understanding of gas hydrate inhibition and promotion. For this reason, we believe that the findings reported here for CO_2 gas hydrate are applicable for CH_4 gas hydrate as well. However, to verify this point, it would require further investigations in the future works.

4 Conclusions

We have successfully conducted the combined kinetic experiments, spectroscopic measurements, and computer simulation to study the effect of TBAB on CO_2 gas hydrate formation and its underlying mechanisms. The kinetic data show an unexpected inhibition observed at extremely small concentration of TBAB (around 0.125% by wt.) besides the commonly known effect of TBAB on the promotion of gas hydrate formation reported for high TBAB concentration regime. The insightful observations from both interface-specific SFG spectra and bulk-specific ATR-FTIR spectra with the support from MD simulation have revealed the critical role of water alignment at interfaces under the influence of surface adsorption of TBA^+ cations in inhibiting gas hydrate formation in dilute TBAB solution. It is suggested that the disordered water induced by residing-in-the-bulk TBA^+ promotes CO_2 gas hydrate formation in solutions of TBAB of high concentration. We explain our findings based on the concept of activation energy of rearrangement of water network during gas hydrate formation. The outcome of this work provides a better understanding of the use of the additives in controlling gas hydrate formations, emerging methods for separation, storage and sequestration of gases.

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