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Full Length Article

Unexpected inhibition of CO_2 gas hydrate formation in dilute TBAB solutions and the critical role of interfacial water structure

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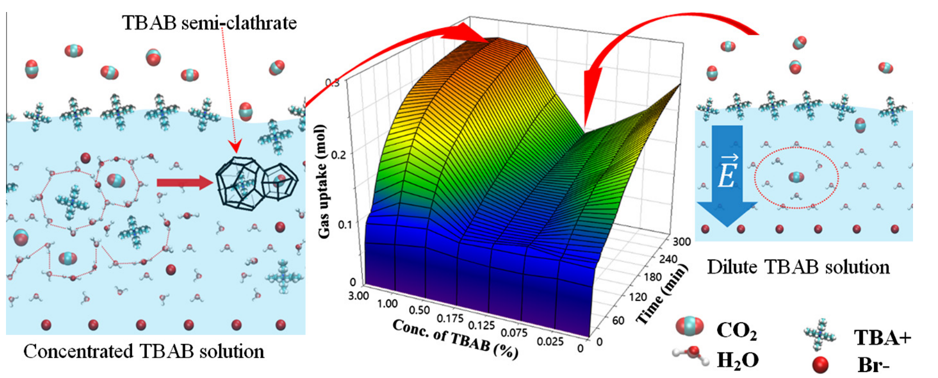
HIGHLIGHTS

- TBAB can promote or inhibit CO_2 gas hydrate formation.
- Water alignment underneath adsorption layer of TBA^+ gives rise to the inhibition.
- Water perturbation by TBA^+ in the bulk gives rise to the promotion.
- Interfacial water is of crucial importance to gas hydrate formation.

GRAPHICAL ABSTRACT



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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 CO_2 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 CO_2 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.

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.

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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 CO_2 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 Reflectance 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 MΩ 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 CO_2 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 $AgGaS_2$ 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 $\alpha_{vis} = 60°$ and that of the IR set to $\alpha_{IR} = 54°$. 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 Reflectance 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 (Themo 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 Å $\leqslant z \leqslant$ 85 Å zone and gas occupied the rest of the box. This configuration means that there were two gas/solution interfaces positioning at $z_{low} = 15$ Å and $z_{high} = 85$ 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 2 fs 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.