Effects of Additives on the Formation of Methane and Carbon Dioxide Gas Hydrates

Nguyen Ngoc Nguyen

B.E. & M.Sc. of Chemical Engineering

A thesis submitted for the degree of Doctor of Philosophy at

The University of Queensland in 2017

School of Chemical Engineering
Abstract

Gas hydrates (GHs) are ice-like crystalline solids comprising water and suitable gases in which gas molecules are physically encaged in a cage-like hydrogen-bonded structure formed by water molecules. Under the presence of appropriate additives, the formation of GHs can be controlled in a desired manner thereby opening novel ways of using GHs for gas storage and transportation, carbon dioxide sequestration, gas separation, desalination, etc. Although significant works have been undertaken to investigate the effects of additives on gas hydrate formation, there still remains a substantial gap in the understanding of the fundamentals behind the experimental observations.

This thesis aims to provide new molecular insights into the effects of surfactants, hydrophobic solid surfaces and sodium halides on the formation of GHs. These effects are studied at the molecular level using synergic combinations of experimental and computational techniques. Kinetics experiments using a high-pressure reactor are carried out to quantify the effect of additives on the kinetics of gas enclathration. A see-through reactor is used for in situ visual observations of the effects of the hydrophobicity of solid surfaces on the formability of GHs. Interface-susceptible sum frequency generation (SFG) vibrational spectroscopy is employed to analyse water structure at gas-solution interfaces. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) is employed to analyse water structure in the bulk solution. Molecular dynamics (MD) simulation is used to calculate surface adsorption of surfactants, concentration profiles, interfacial water alignment, water ordering and local concentration of gases. The results from kinetics measurements are correlated with the spectroscopic and simulation data to unravel the molecular mechanisms underlying the experimental observations.

The key findings of this thesis are as follows. First, surfactants display an extraordinary inhibition of gas hydrate formation at ultralow concentrations (e.g., 0.3 mM for sodium dodecyl sulfate and 3.6 mM for tetra-butyl ammonium bromide) beside the well-known promotion effect in high concentration regime. The analysis of water structure based on SFG and MD results reveals a strong alignment of water underneath surface adsorption of surfactants which gives rise to the extraordinary inhibition effect. The perturbation of water structure in the bulk by bulk-residing surfactants gives rise to the promoted gas hydrate formation in concentrated surfactants solutions. Secondly, when one hydrophobic solid surface and one hydrophilic solid surface are placed simultaneously in a see-through reactor, in situ visual observations show a preferential formation of CO₂ hydrate at a hydrophobic solid surface. The analysis of MD results reveals an interfacial gas enrichment and a structured water network both happening at the hydrophobic solid surface, in contrast with an interfacial gas depletion and a disrupted water network happening at the
hydrophilic solid surface. This finding uncovers the origin of the promoted hydrate formation in the presence of hydrophobic solid surfaces (including dry water) to be the interfacial gas enrichment and the structured water network at the hydrophobic solid-water interface. Finally, it is very interesting that sodium halides can act as hydrate promoters when they are used at low concentrations (50 — 70 mM). In high-concentration regime, the salts become effective hydrate inhibitors as expected. The analysis of this result using the concept of ion-specific effect points out that such anomalous promotion effect originates from the hydrophobic nature of large-size and low-charge-density halide ions (e.g., I⁻ and Br⁻). All of these findings ultimately infer that the formation of GHs is actually governed by the additives-induced change in local water structure, especially water structure at the interfaces. The additives-induced change in local water structure, in turn, is governed by the hydrophobic effect. From this new perspective, this thesis develops a hypothesis of hydrophobic effect on gas hydrate formation in the presence of additives, which serves as a universal explanation for the effects of additives on gas hydrate formation.

In summary, this thesis sheds new molecular insights into the effects of interfacial water alignment, hydrophobic hydration, hydrophobic interaction and ions-specificity on the formation of GHs. It provides steps towards mastering hydrate-based processes in many industrial and environmental applications.
Declaration by author

This thesis is composed of my original work, and contains no material previously published or written by another person except where due reference has been made in the text. I have clearly stated the contribution by others to jointly-authored works that I have included in my thesis.

I have clearly stated the contribution of others to my thesis as a whole, including statistical assistance, survey design, data analysis, significant technical procedures, professional editorial advice, and any other original research work used or reported in my thesis. The content of my thesis is the result of work I have carried out since the commencement of my research higher degree candidature and does not include a substantial part of work that has been submitted to qualify for the award of any other degree or diploma in any university or other tertiary institution. I have clearly stated which parts of my thesis, if any, have been submitted to qualify for another award.

I acknowledge that an electronic copy of my thesis must be lodged with the University Library and, subject to the policy and procedures of The University of Queensland, the thesis be made available for research and study in accordance with the Copyright Act 1968 unless a period of embargo has been approved by the Dean of the Graduate School.

I acknowledge that copyright of all material contained in my thesis resides with the copyright holder(s) of that material. Where appropriate I have obtained copyright permission from the copyright holder to reproduce material in this thesis.
Publications during candidature


Publications included in this thesis


<table>
<thead>
<tr>
<th>Contributor</th>
<th>Statement of contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ngoc N. Nguyen</td>
<td>Designed experiments: 80%</td>
</tr>
<tr>
<td></td>
<td>Performed experiments: 80%</td>
</tr>
<tr>
<td></td>
<td>Designed simulations: 85%</td>
</tr>
<tr>
<td></td>
<td>Performed simulations: 100%</td>
</tr>
<tr>
<td></td>
<td>Analysed data: 70%</td>
</tr>
<tr>
<td></td>
<td>Wrote the paper: 90%</td>
</tr>
<tr>
<td></td>
<td>Edited the papers: 70%</td>
</tr>
<tr>
<td></td>
<td>Ngoc N. Nguyen was the main contributor who was principally responsible for designing and performing all experiments and simulations, analysing data, writing and editing the paper</td>
</tr>
<tr>
<td>Anh V. Nguyen</td>
<td>Designed experiments: 20%</td>
</tr>
<tr>
<td></td>
<td>Performed experiments: 0%</td>
</tr>
<tr>
<td></td>
<td>Designed simulations: 10%</td>
</tr>
<tr>
<td></td>
<td>Performed simulations: 0%</td>
</tr>
<tr>
<td></td>
<td>Analysed data: 20%</td>
</tr>
<tr>
<td></td>
<td>Wrote the paper: 10%</td>
</tr>
<tr>
<td></td>
<td>Edited the papers: 20%</td>
</tr>
<tr>
<td></td>
<td>Anh V. Nguyen was the principal academic advisor who contributed to designing experiments and simulations, analysing data, writing and critically editing the paper</td>
</tr>
<tr>
<td>Khoi T. Nguyen</td>
<td>Designed experiments: 0%</td>
</tr>
<tr>
<td></td>
<td>Performed experiments: 10%</td>
</tr>
<tr>
<td></td>
<td>Designed simulations: 0%</td>
</tr>
<tr>
<td></td>
<td>Performed simulations: 0%</td>
</tr>
<tr>
<td></td>
<td>Analysed data: 0%</td>
</tr>
<tr>
<td></td>
<td>Wrote the paper: 0%</td>
</tr>
<tr>
<td></td>
<td>Edited the papers: 0%</td>
</tr>
<tr>
<td></td>
<td>Khoi T. Nguyen contributed to the measurement of SFG spectra</td>
</tr>
</tbody>
</table>
| Llew Rintoul | Designed experiments: 0%  
|             | Performed experiments: 10%  
|             | Designed simulations: 0%  
|             | Performed simulations: 0%  
|             | Analysed data: 10%  
|             | Wrote the paper: 0%  
|             | Edited the papers: 0%  
|             | Llew Rintoul contributed to the measurement and analysis of ATR-FTIR spectra |
| Liem X. Dang | Designed experiments: 0%  
|             | Performed experiments: 0%  
|             | Designed simulations: 5%  
|             | Performed simulations: 0%  
|             | Analysed data: 0%  
|             | Wrote the paper: 0%  
|             | Edited the papers: 10%  
|             | Liem X. Dang contributed to designing simulations and editing the paper |
Nguyen, N. N.; Nguyen, A. V.; Dang, L. X., The Inhibition of Methane Hydrate Formation by Water Alignment underneath Surface Adsorption of Surfactants. *Fuel* 2017, **197**, 488-496. – incorporated as Chapter 6

<table>
<thead>
<tr>
<th>Contributor</th>
<th>Statement of contribution</th>
</tr>
</thead>
</table>
| Ngoc N. Nguyen | Designed experiments: 80%  
|               | Performed experiments: 100%  
|               | Designed simulations: 85%  
|               | Performed simulations: 100%  
|               | Analysed data: 80%  
|               | Wrote the paper: 90%  
|               | Edited the papers: 70%  
|               | Ngoc N. Nguyen was the main contributor who was principally responsible for designing and performing all experiments and simulations, analysing data, writing and editing the paper |
| Anh V. Nguyen | Designed experiments: 20%  
|               | Performed experiments: 0%  
|               | Designed simulations: 10%  
|               | Performed simulations: 0%  
|               | Analysed data: 20%  
|               | Wrote the paper: 10%  
|               | Edited the papers: 20%  
|               | Anh V. Nguyen was the principal academic advisor who contributed to designing experiments and simulations, analysing data, writing and critically editing the paper |
| Liem X. Dang  | Designed experiments: 0%  
|               | Performed experiments: 0%  
|               | Designed simulations: 5%  
|               | Performed simulations: 0%  
|               | Analysed data: 0%  
|               | Wrote the paper: 0%  
|               | Edited the papers: 10%  
|               | Liem X. Dang contributed to designing simulations and editing the paper |

<table>
<thead>
<tr>
<th>Contributor</th>
<th>Statement of contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ngoc N. Nguyen</td>
<td>Designed experiments: 80%</td>
</tr>
<tr>
<td></td>
<td>Performed experiments: 100%</td>
</tr>
<tr>
<td></td>
<td>Designed simulations: 80%</td>
</tr>
<tr>
<td></td>
<td>Performed simulations: 100%</td>
</tr>
<tr>
<td></td>
<td>Analysed data: 50%</td>
</tr>
<tr>
<td></td>
<td>Wrote the paper: 70%</td>
</tr>
<tr>
<td></td>
<td>Edited the papers: 60%</td>
</tr>
<tr>
<td></td>
<td>Ngoc N. Nguyen was the main contributor who was principally responsible for designing and performing all experiments and simulations, analysing data, writing and editing the paper</td>
</tr>
<tr>
<td>Anh V. Nguyen</td>
<td>Designed experiments: 10%</td>
</tr>
<tr>
<td></td>
<td>Performed experiments: 0%</td>
</tr>
<tr>
<td></td>
<td>Designed simulations: 10%</td>
</tr>
<tr>
<td></td>
<td>Performed simulations: 0%</td>
</tr>
<tr>
<td></td>
<td>Analysed data: 10%</td>
</tr>
<tr>
<td></td>
<td>Wrote the paper: 10%</td>
</tr>
<tr>
<td></td>
<td>Edited the papers: 20%</td>
</tr>
<tr>
<td></td>
<td>Anh V. Nguyen was the principal academic advisor who contributed to designing experiments and simulations, analysing data, writing and critically editing the paper</td>
</tr>
<tr>
<td>Karen M. Steel</td>
<td>Designed experiments: 10%</td>
</tr>
<tr>
<td></td>
<td>Performed experiments: 0%</td>
</tr>
<tr>
<td></td>
<td>Designed simulations: 0%</td>
</tr>
<tr>
<td></td>
<td>Performed simulations: 0%</td>
</tr>
<tr>
<td></td>
<td>Analysed data: 0%</td>
</tr>
<tr>
<td></td>
<td>Wrote the paper: 0%</td>
</tr>
<tr>
<td></td>
<td>Edited the papers: 10%</td>
</tr>
<tr>
<td></td>
<td>Karen M. Steel contributed to designing experiments and editing the paper</td>
</tr>
</tbody>
</table>
| Liem X. Dang | Designed experiments: 0%  
Performed experiments: 0%  
Designed simulations: 10%  
Performed simulations: 0%  
Analysed data: 0%  
Wrote the paper: 0%  
Edited the papers: 0%  
Liem X. Dang contributed to designing simulations and editing the paper |
|---|---|
| Mirza Galib | Designed experiments: 0%  
Performed experiments: 0%  
Designed simulations: 0%  
Performed simulations: 0%  
Analysed data: 40%  
Wrote the paper: 10%  
Edited the papers: 0%  
Mirza Galib made a major contribution to the calculation and analysis of water structure near solid surfaces |

<table>
<thead>
<tr>
<th>Contributor</th>
<th>Statement of contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ngoc N. Nguyen</td>
<td>Designed experiments: 90%</td>
</tr>
<tr>
<td></td>
<td>Performed experiments: 100%</td>
</tr>
<tr>
<td></td>
<td>Analysed data: 80%</td>
</tr>
<tr>
<td></td>
<td>Wrote the paper: 80%</td>
</tr>
<tr>
<td></td>
<td>Edited the papers: 70%</td>
</tr>
<tr>
<td></td>
<td>Ngoc N. Nguyen was the main contributor who was principally responsible for designing and performing all experiments, analysing data, writing and editing the paper</td>
</tr>
<tr>
<td>Anh V. Nguyen</td>
<td>Designed experiments: 10%</td>
</tr>
<tr>
<td></td>
<td>Performed experiments: 0%</td>
</tr>
<tr>
<td></td>
<td>Analysed data: 20%</td>
</tr>
<tr>
<td></td>
<td>Wrote the paper: 20%</td>
</tr>
<tr>
<td></td>
<td>Edited the papers: 30%</td>
</tr>
<tr>
<td></td>
<td>Anh V. Nguyen was the principal academic advisor who contributed to designing experiments, analysing data, writing and critically editing the paper</td>
</tr>
</tbody>
</table>


<table>
<thead>
<tr>
<th>Contributor</th>
<th>Statement of contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ngoc N. Nguyen</td>
<td>Performed literature review: 100%</td>
</tr>
<tr>
<td></td>
<td>Wrote the paper: 90%</td>
</tr>
<tr>
<td></td>
<td>Ngoc N. Nguyen was the main contributor who was principally responsible for designing the paper, writing and editing the paper</td>
</tr>
<tr>
<td>Anh V. Nguyen</td>
<td>Performed literature review: 0%</td>
</tr>
<tr>
<td></td>
<td>Wrote the paper: 10%</td>
</tr>
<tr>
<td></td>
<td>Anh V. Nguyen was the principal academic advisor who contributed to academic guidance, writing and critically editing the paper</td>
</tr>
</tbody>
</table>
Contributions by others to the thesis

No contributions by others

Statement of parts of the thesis submitted to qualify for the award of another degree

None
Acknowledgements

First of all, I would like to give a special thanks to my principal supervisor, Professor Anh V. Nguyen. Your unreserved support and great guidance are essential for my successes in the scholarship application and the performance of my PhD candidature. In addition to the academic supervision, you also gave me invaluable advices for shaping my career and my life. Indeed, no word is adequate to express my gratitude for Professor Anh for doing all of these things for me. I would like to thank also my associate supervisor, Dr. Karen M. Steel, for your valuable advice, guidance and encouragement. Your friendliness and kindness are very influential to me and I really appreciate that. I wish to expand my gratitude to my academic committee members, Professor Victor Rudolph, A/Professor Tony Howes; your academic support, recommendations and discussions during my candidature are fruitful to the success of my PhD journey. Without the time and efforts from all of you, my PhD would have not been possible.

I gratefully acknowledge the Australian Government for awarding me the Australian Awards Scholarship. I thank The University of Queensland (UQ) and School of Chemical Engineering for providing me an excellent studying environment. I express my appreciation to all UQ academic and administrative staff, my colleagues and fellows for being helpful and responsible whenever I need help.

Specially, I owe a deep gratitude to my parents, my wife, my little son and all my family relatives who always support and stimulate me in my PhD journey. They are indeed co-travelers with me in this adventurous PhD journey. Last but not least, I am grateful to Dr. Liem Dang and Dr. Mirza Galib (Pacific Northwest National Laboratory, USA), Dr. Llew Rintoul (QUT, Australia), Dr. Tuan H. A. Nguyen, Dr. Faezeh Farhang and Mr. Trung Tran (UQ) for making my PhD journey more meaningful and memorable.
Keywords
gas hydrate, carbon capture and storage, gas storage, water structure, hydrophobic effect, surfactant effect, SFG spectroscopy, hydrate promotion, hydrate inhibition

Australian and New Zealand Standard Research Classifications (ANZSRC)
ANZSRC code: 090499 Chemical Engineering not elsewhere classified, 70%
ANZSRC code: 090799 Environmental Engineering not elsewhere classified, 30%

Fields of Research (FoR) Classification
FoR code: 0904 Chemical Engineering, 70%
FoR code: 0907 Environmental Engineering, 30%
Table of Contents

Abstract ................................................................................................................................. i
Declaration by author ........................................................................................................ iii
Publications during candidature........................................................................................ iv
Publications included in this thesis ..................................................................................... v
Acknowledgements ............................................................................................................ xii
Keywords ............................................................................................................................ xiii
Australian and New Zealand Standard Research Classifications (ANZSRC) ....................... xiii
Fields of Research (FoR) Classification ............................................................................ xiii
List of Figures .................................................................................................................... xix
List of Tables ...................................................................................................................... xxvii
List of Abbreviations used in this thesis ............................................................................ xxviii
1 Chapter 1: Introduction .................................................................................................... 1
2 Chapter 2: Literature review ........................................................................................... 4
   2.1 Gas clathrate hydrates ............................................................................................. 4
   2.2 The formation of gas hydrates ................................................................................. 6
      2.2.1 Macroscopic description and molecular concepts ........................................... 6
      2.2.2 The formation of gas hydrate at the interface ............................................... 8
   2.3 The significance of gas hydrates .............................................................................. 9
      2.3.1 Gas hydrates in energy sector ......................................................................... 10
      2.3.2 Gas hydrates and the environment .................................................................. 11
      2.3.3 Gas hydrates for industrial productions ......................................................... 11
   2.4 The effects of additives on gas hydrate formation .................................................. 12
      2.4.1 The effects of thermodynamic inhibitors ....................................................... 12
      2.4.2 The effects of low-dosage hydrate inhibitors on gas hydrate formation .......... 13
      2.4.3 Surfactants effects on gas hydrate formation ................................................. 14
      2.4.4 The effects of hydrophobic particles on gas hydrate formation ..................... 19
2.5 The knowledge gaps in the current literature ......................................................... 21

Chapter 3: Research Objectives and Hypotheses .......................................................... 30
3.1 The objectives of this research ................................................................................... 30
3.2 Hypotheses and research designs ............................................................................ 31

Chapter 4: Experimental Apparatus and Computational Methods ............................... 34
4.1 Gas hydrate kinetics experiments using a high-pressure reactor ............................... 34
4.2 Induction time, gas uptake and growth rate of gas hydrate formation ...................... 35
4.3 Visual observation of hydrate formation using a see-through reactor ....................... 36
4.4 Sum Frequency Generation vibrational spectroscopy .............................................. 37
4.5 Attenuated total reflectance Fourier-transform infrared spectroscopy .................... 38
4.6 Molecular dynamics simulation .............................................................................. 38
4.6.1 Simulation of gas-solution interfaces .................................................................... 39
4.6.2 Simulation of solid-water interfaces ..................................................................... 40
4.6.3 Simulation of contact angle .................................................................................. 42

Chapter 5: Unexpected inhibition of CO₂ hydrate formation in dilute TBAB solution and
the critical role of the interfacial water structure ......................................................... 45
5.1 Background context .................................................................................................. 46
5.2 Unexpected inhibition of CO₂ hydrate formation in dilute TBAB solutions ............. 46
5.3 The effect of TBAB on water structure ..................................................................... 49
5.3.1 Dual effect of TBAB on water structure at the gas-solution interface ................. 49
5.3.2 Effect of TBAB on water structure in the bulk ..................................................... 50
5.3.3 Results of molecular dynamic (MD) simulation .................................................. 52
5.4 General discussion ................................................................................................... 54
5.5 Conclusion ............................................................................................................... 55

Chapter 6: The inhibition of methane hydrate formation by water alignment underneath
surface adsorption of surfactants .................................................................................. 58
6.1 Background context ................................................................................................ 59
11 Appendix ............................................................................................................................................. 136

11.1 Supporting information for Chapter 5 ............................................................................................... 136

11.1.1 Surface adsorption of TBA$^+$ cation evidenced from SFG spectra ........................................ 136

11.1.2 Correlation between TBAB concentration and area of CH bend ............................................ 136

11.1.3 Calculation of local concentration and surface excess in MD simulation .................. 137

11.2 Supporting information for Chapter 6 .............................................................................................. 138

11.2.1 Modulus fitting of SFG spectra ................................................................................................. 138

11.2.2 The effect of mixing solution on SFG spectra .......................................................................... 139

11.3 Supporting information for Chapter 7 .......................................................................................... 140

11.3.1 The movement of gas molecules to the interfaces ............................................................. 140

11.3.2 The effect of initial concentration of gas on the density of gas at the interface . 140

11.3.3 Instantaneous interface and density of water ......................................................................... 141

11.4 Supporting information for Chapter 8 .......................................................................................... 142

11.4.1 Determination of salt concentration and hydrophobicity ................................................... 142

11.5 List of chemicals used or mentioned in this thesis ...................................................................... 142
List of Figures

**Figure 2.1** The constitution of three common structures of gas hydrates [3]. Depending on the sizes and compositions of the guests, the resulting clathrate can have one of three crystal structure as indicated. The most common hydrate formers of each structure are also shown. ................................. 5

**Figure 2.2** A typical T-P graph showing different stages involved in gas hydrate formation process. The guest used was methane. The experiment was conducted in an isochoric reactor at initial pressure of 7.5 MPa and target temperature set to 0.5°C. .................................................. 7

**Figure 2.3** Mechanism of gas hydrate formation through labile clusters hypothesis as reproduced from Sloan et al [1]. Different stages of gas enclathration process are explained in the figure. .......... 8

**Figure 2.4** The formation of a methane hydrate thin film at a methane-water interface [41]. The initiation and propagation of a thin hydrate film on droplet’s surface is clearly shown. .............. 9

**Figure 2.5** Methane hydrate formation at methane-water interface [42]. Three proposed steps are indicated in the figure. ........................................................................................................ 9

**Figure 2.7** Hydrate-based gas separation for the capture of CO$_2$ from flue gas. The selective formation of CO$_2$ hydrate separates this gas from the mixture. Then the dissociation of CO$_2$ hydrate in the next stage produces CO$_2$ stream and spent water. The spent water is recycled to hydrate formation stage........................................................................................................ 12

**Figure 2.8** Physicochemical characteristics of surfactants: Amphiphilic structure of SDS surfactant (a); dodecyl sulfate (DS$^-$) adsorption on solution surface and DS$^-$ micelle formation in the bulk (b); the Krafft point of SDS surfactant (c). On Figure (b), the gas phase and the counter ions (Na$^+$) are omitted for clarity. ................................................................. 15

**Figure 2.9** Illustration of a SDS surfactant micelle in ethane hydrate-forming system as reproduced from Zhong et al. [87]. The surfactant micelle is thought to act as a minute gas reservoir thereby facilitates the gas hydrate formation. The grey area in the figure indicates the interior space with high density of ethane ........................................................................................................ 17

**Figure 2.10** Contact angle as a measure of hydrophobicity of a solid surface ........................................ 19

**Figure 4.1** The scheme of the experiment setup (left) and the real image of the high-pressure reactor and its accessories (right)........................................................................................................ 34

**Figure 4.2** The determination of the induction time of gas hydrate formation. Here, the guest used was methane. The experiment was conducted in an isochoric reactor at initial pressure of 7.5 MPa and target temperature set to 0.5°C. ........................................................................................................ 35
**Figure 4.3** The scheme of experiment setup for studying effects of surface hydrophobicity on gas hydrate formation: (a) the setup of the whole system and (b) the configuration of modified glass surfaces in the hydrate formation cell and their surface hydrophobicity as shown by contact angle.

**Figure 4.4** Sampling system for recording SFG signal for methane-solution interface, consisting of: cell cap (1), cell base (2), sample base (3), solution (4), transparent CaF$_2$ crystal windows (5), O-ring (5), inlet (7) and outlet (8) of methane stream.

**Figure 4.5** Example of a simulation box for study the gas-solution interface. In this example, the additive is tetra-butyl ammonium bromide which consists of tetra-butyl ammonium (TBA$^+$) cation and Br$^-$ anion. The system has two gas-solution interfaces at $z_{\text{low}} = 15$ Å and $z_{\text{high}} = 85$ Å. The gas molecules are hidden for clarity.

**Figure 4.6** The definition of $\phi$ in this work.

**Figure 4.7** A scheme of a real alkyl-grafted solid surface (a) and an example of simulated hydrophobic solid-water interface built for my simulation (b). The fixed hydrocarbon layer in simulation box (image b) is to mimic the alkyl-grafted layer in the real system (image a). For the image (b), it is noted that this is the initial configuration, and it only shows the bottom part of simulation box (as the top part is truncated for better clarity of the interface).

**Figure 4.8** The method for determining the contact angle between a simulated solid surface and a water droplet. Simulation snapshot (left) show an instantaneous shape of the water droplet on simulated surface. Some vaporised water molecules are seen from this snapshot. The density profile of the water droplet (right) shows the mean boundary of the droplet. The contact angle is estimated by extrapolating the fitting curve to the solid surface, as indicated.

**Figure 5.1** Typical changes in the instantaneous pressure ($P$) and temperature ($T$) versus time for CO$_2$ hydrate formation. The concentration used was 3% TBAB (by weight). The second drop in $P$ and the rise in $T$ provide strong evidence of the exothermal formation of CO$_2$ hydrate.

**Figure 5.2** Experimental results for CO$_2$ uptake versus TBAB concentration and time: The dual effect of TBAB on the formation of CO$_2$ hydrate. 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 CO$_2$ 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.
Figure 5.3 The rate of CO₂ 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 that the growth rate in solutions of high TBAB concentrations. ................................................................. 49

Figure 5.4 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 (the peak height) at low TBAB concentrations manifests the increasing alignment of water at the surface of dilute TBAB solutions. The decrease in the SFG amplitude signal at high TBAB concentration shows that water became less aligned at the surface of concentrated solution compared to that of dilute TBAB solutions. .............................................................. 50

Figure 5.6 Simulation box for study surface adsorption of TBA⁺ cations at gas-solution interfaces. The x, y, z dimensions of the box were 50Å, 50Å, 100Å, respectively. Two gas-solution interfaces located at z low = 15Å and z high = 85Å. The TBA⁺ and Br⁻ ions were initially inserted randomly into the aqueous zone of the simulation box. The gas phase is hidden for a better clarity. ...................... 52

Figure 5.7 The results of MD 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 aqueous phase 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. ........................................................................................................... 53

Figure 6.1 Typical P-T profile showing the change in pressure and temperature versus time during methane hydrate formation. The experiment was performed in an isochoric system. The initial pressure was 75 atm (7.5 MPa) and the target temperature was set to 0.5 ⁰C ........................................ 60

Figure 6.2 Induction time of methane hydrate formation in SDS solution of different concentrations. The data show an extraordinary inhibition observed at the concentration around 0.3 mM, along with a well-known promotion observed in concentrated SDS solution. ...................... 61

Figure 6.3 Time-dependent methane uptake by hydrate formation in SDS solution of different concentrations. A blue bay shows a domain of low methane uptake in the concentrations between 0.05 mM and 0.5 mM. In high concentration region, the colour profile becomes red after few minutes, indicating the promoted hydrate formation with high methane uptake. ......................... 62
**Figure 6.4** The data from SFG spectra. (a): a typical of experimental SFG spectra and its fitting components, and (b): the intensity of each component peak and the ratio between them as a function of SDS concentration. From graph (b), strong hydrogen bonds of water at the surface of 0.3 mM SDS solution is evidenced.

**Figure 6.5** An example of the initial configuration of simulation box for a methane-solution interface. At the beginning of the simulation, SDS surfactant (DS\(^{-}\) and Na\(^{+}\)) were inserted randomly in the aqueous phase with water. Methane molecules were in the gas phase.

**Figure 6.6** Properties of methane-solution interface obtained from simulation. (a) An example of interfacial properties calculated from simulation and (b) the dependence of orientational parameter upon the total concentration of SDS in simulation box. The total concentration is defined as the molar amount of SDS divided by the volume of the aqueous phase in simulation box (in liter).

**Figure 6.7** Typical snapshots of methane-solution interface from my simulation. These are representative configurations of the equilibrium state of the interfaces. Only water and DS\(^{-}\) anions are shown. The gas phase and Na\(^{+}\) cations are hidden for clarity. Panels (a), (b) and (c) are for the Systems A, B and C, respectively.

**Figure 6.8** The effect of mixing surfactants on the induction time of methane hydrate formation and interfacial water alignment. Although both 0.3 mM SDS solution and 3.6 mM TBAB are strong inhibitors individually, the mixed solution of 0.3 mM SDS and 3.6 mM TBAB is an effective promoter. The ration I(s)/I(w) is smaller in the mixed surfactant solution compared to those in the solutions of single surfactant.

**Figure 6.9** The correlation between methane hydrate kinetics and interfacial water alignment in SDS solution. The data evidently show that a higher degree of interfacial water alignment results in slower hydrate formation kinetics.

**Figure 6.10** The hydration of methane in ordinary water (a) and aligned water (b). The hydrogen bonds between water molecules on hydration shells are shown. The dark spheres with a negative sign on indicate the head group of surfactant. The surfactant-induced alignment of water results in an unfavourable condition for the hydration of methane (b).

**Figure 7.1** Simulation system of solid-water interface. A solid was in contact with water to form the interface. CH\(_4\) molecules, for example, were inserted randomly in water phase to simulate dissolved methane.

**Figure 7.2** Simulation results for contact angle (θ) of a water droplet on a simulated hydrophobic (OTA) surface and hydrophilic (COO) surface. The equilibrium contact angles for the OTA and...
COO surfaces are 125° and 0°, respectively. The dashed line indicates the contact angle that was determined using the VMD software. The contact angle was assigned to 0° when the water droplet (on the COO surface) spread out completely, resulting in a water layer on the surface. .......................... 76

**Figure 7.3** Density profiles of gas and water near a hydrophobic solid surface: (a) CH₄ system and (b) CO₂ system. The blue solid curves are the fitting of water density using tanh function. These is a similarity between these two gases except no evidence of a gas dense layer for CO₂. The initial concentration of gas (both CH₄ and CO₂) is 1.39 M or 210 gas molecules per 5400 water molecules. For clarity, the constant density profiles beyond 18Å of Δz are not shown. ........................................ 78

**Figure 7.4** Density profiles of gas and water near hydrophilic solid surface: (a) CH₄ system and (b) CO₂ system. The formation of a hydration layer at a hydrophilic surface is evidenced. Gas is expelled from a hydrophilic surface as shown by a narrow depletion in the gas density profile. ..... 78

**Figure 7.5** Probability density distribution of the coordination number (a, c) and hydrogen bonds (b, d) formed by a water molecule at the interface and the bulk. Some terminologies are self-explained in the figures. Probability density are not normalised to the density of water molecules for the bulk and the interface. Coordination number was defined as the number of water molecules found within 3.2 Å of the central water molecule. Hydrogen bond was defined by the distance and angle criteria (O─O distance of 3.45 Å and O_dx─H─O_y angle of 30°). ........................................ 80

**Figure 7.6** Probability density distribution of the tetrahedrality order parameter q₃ and q₄ (a, b), and d₃₄ and d₄₅ (c, d) for water molecules at the interface and in the bulk for the hydrophobic surface with water. Interface region 1 encompasses the region within 3.2 Å from the instantaneous interface. Likewise, Interface region 2 is between 3.2 Å and 5.5 Å. The bulk is beyond the distance 5.5 Å. Probability densities are not normalised to the density of water molecules for the bulk and the interface. ................................................................. 82

**Figure 7.7** Probability density distribution of the tetrahedrality order parameter q₃ (a) and q₄ (b) for water molecules at the interface and in the bulk for the hydrophilic surface with water. Interface region 1 encompasses the region within 3.2 Å from the instantaneous interface. Likewise, Interface region 2 is between 3.2 Å and 5.5 Å. The bulk is beyond the distance 5.5 Å. Probability densities are not normalised to the density of water molecules for the bulk and the interface. .......................... 83

**Figure 7.8** The preferential formation of CO₂ hydrate on the hydrophobic surface under quiescent condition. (a) shows the image of the solid-water interfaces before pressurization; the insets show the contact angles of water droplets on the modified solid surfaces. (b) shows the interfaces after 1 h of pressurization. (c) shows the interfaces after 12 h of pressurization: a hydrate crystal was formed
on the hydrophobic surface but no hydrate was observed on the hydrophilic surface. Experiments were conducted at 6 MPa and 1°C .................................................................................................................. 84

**Figure 7.9** Preferential formation of CO$_2$ hydrate on a hydrophobic surface under stirring of water. .......................................................................................................................... 84

**Figure 7.10** Formation of CO$_2$ gas bubbles on a hydrophobic surface (left) and on a hydrophilic surface (right). On the hydrophobic surface, gas bubbles nucleate and grow very intensively but there are only a few bubbles formed slowly on the hydrophilic surface. ........................................ 85

**Figure 7.11** Graphical illustration of gas density profile at the interfacial regions of the hydrophobic solid-water and hydrophilic solid-water interfaces, in comparison with those in the bulk. The interfacial gas enrichment at a hydrophobic surface is attributed to the origin of gas hydrate promotion by hydrophobic solid particles. .................................................................................................................. 87

**Figure 8.1** Pressure (solid lines) and temperature (dashed lines) versus time during methane hydrate formation in sodium iodide solutions of different concentrations. The pressure and temperature at zero time were 1465 psi (10 MPa) and 24-25 °C, respectively. The target temperature was set to be 1.5°C. .......................................................................................................................... 92

**Figure 8.2** Effect on sodium halides and their concentration on methane consumption versus time. The water line divides the curves into two groups, showing the dual effect of sodium halides on the formation of methane gas hydrate: sodium halides promote gas hydrate formation at low concentration whereas they become an inhibitor at higher concentration. ........................................ 93

**Figure 8.3** Effect of sodium halides and concentration on growth rate of methane hydrate versus time. The blue line for water is shown as a reference. .................................................................................................................. 94

**Figure 8.4** Dependence of maximum gas consumption (top) and induction time (bottom) on sodium halides and their concentrations. The induction times at high concentrations of NaCl and NaF are extremely (infinitely) long.......................................................... 96

**Figure 8.5** Conceptual diagram of the formation of clathrate cages via hydrophobic hydration. .... 98

**Figure 9.1** A typical T-P graph showing different stages involved in gas hydrate formation process. The guest used was methane. The experiment was conducted in an isochoric reactor at initial pressure of 7.5 MPa and target temperature set to 0.5°C [20]. ............................................................. 106

**Figure 9.2** Mechanism of gas hydrate formation through labile clusters hypothesis [1]. ........... 107

**Figure 9.3** The formation of a methane hydrate thin film at a methane-water interface [39]. The initiation and propagation of a methane hydrate film is clearly observed on the water droplet’s surface........................................................................................................................................ 108
**Figure 9.4** Methane hydrate formation at methane-water interface [40]. Three steps involved are shown on the figure. 

**Figure 9.5** The amphiphilic structure of SDS surfactant (a); dodecyl sulfate (DS\(^-\)) adsorption on solution surface and DS\(^-\) micelle formation in bulk (b); the Krafft point of SDS surfactant (c). On Figure (b), the gas phase and the counter ions (Na\(^+\)) are omitted for clarity. 

**Figure 9.6** Illustration of a SDS surfactant micelle in ethane hydrate-forming system [81]. The surfactant micelle is thought to act as a minute gas reservoir thereby facilitates the gas hydrate formation. The grey area in the figure indicates the interior space with high density of ethane. 

**Figure 9.7** Contact angle as a measure of hydrophobicity of a solid surface. 

**Figure 9.8** Hypothesis of hydrophobic effect on gas hydrate formation in the presence of a hydrophobic additive. 

**Figure 9.9** The effects of hydrocarbon chain length (hydrophobicity) of tetra-alkyl ammonium bromide on gas hydrate formation. The single sphere represents the Br\(^-\) counter ion. 

**Figure 9.10** Simulation snapshots show an increased methane concentration near a hydrophobic surface (a) in contrast with a decreased concentration near a hydrophilic surface (b) [132]. 

**Figure 9.11** The explanation of the dual effect of halide ions on gas hydrate formation [48]. Cage-like hydration shells of iodide seed the gas enclathration (middle image). The increased completion for water in concentrated salt solutions inhibits gas enclathration (right image). 

**Figure 9.12** The adsorption of DS\(^-\) anions on the gas-solution interface in ultralow concentration regime (a); the methane enclathration in ordinary water (b) and in the aligned water underneath surface adsorption of surfactants (c) [20]. The negative charges in (c) represent the hydrophilic heads of DS\(^-\). 

**Figure 11.1** SFG spectra of alkyl group. The occurrence of vibrational modes of alkyl group on SFG data evidently indicates the presence of TBA\(^+\) on the surface of solution. 

**Figure 11.2** ATR-FTIR results for the integrated area of CH bend using a local base line versus TBAB concentration. 

**Figure 11.3** An example of density profile of TBA\(^+\) cation and water of System B (containing 15 TBAB molecules) in our simulation. 

**Figure 11.4** The fitting of experimental SFG signals using modulus SFG model. 

**Figure 11.5** The effect of the addition of TBAB on the SFG spectra of SDS solution. The concentrations are shown on the graph.
**Figure 11.6** The time-dependent gas concentration in the interfacial region within 10 Å from hydrophobic solid surface. The increase in the concentration indicates the movement of gas molecules from the bulk to the interface. .......................................................... 140

**Figure 11.7** Density profile versus initial concentration of gas at hydrophobic solid-water interface for (a) CH₄ and (b) CO₂ systems. The results show that interfacial gas enrichment (IGE) depends strongly on the initial concentration of gas as the existence of IGE is governed by dynamic equilibrium. ........................................................................................................................................ 141

**Figure 11.8** Density profile of water as a function of the distance from the instantaneous interface. ........................................................................................................................................................................ 142
List of Tables

**Table 2.1** Unconventional low dosage hydrate inhibitors of increasing interest ........................................ 14
**Table 2.2** Surfactants that are widely used in clathrate hydrate research .................................................. 16
**Table 2.3** Hydrate promotion capability of different surfactants ................................................................. 18
**Table 2.4** The most widely used hydrophobic solid surfaces in gas hydrate formation ......................... 20
**Table 8.1** Contact angle (CA) between salt crystal surfaces and their saturated solutions ............. 100
**Table 8.2** Mass balance showing the salt distribution in methane hydrates .............................................. 101
**Table 9.1** New types of LDHIs reported in the recent literature ................................................................. 111
**Table 9.2** Common surfactants as gas hydrate promoters ................................................................. 113
**Table 9.3** The effectiveness of surfactants in promoting gas hydrate formation ..................................... 115
**Table 9.4** Effects of hydrophobic solid surfaces on gas hydrate formation ............................................. 117
### List of Abbreviations used in this thesis

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AAs</td>
<td>Anti-agglomerants</td>
</tr>
<tr>
<td>AFPs</td>
<td>Antifreeze proteins</td>
</tr>
<tr>
<td>ATR-FTIR</td>
<td>Attenuated total reflectance Fourier transform infrared</td>
</tr>
<tr>
<td>CCS</td>
<td>Carbon capture and storage</td>
</tr>
<tr>
<td>CMC</td>
<td>Critical micellar concentration</td>
</tr>
<tr>
<td>CP</td>
<td>Cyclo-pentane</td>
</tr>
<tr>
<td>DAH</td>
<td>Dodecyl ammonium hydrochloride</td>
</tr>
<tr>
<td>DN2Cl</td>
<td>Dodecylpropane-1,3-diamine hydrochloride</td>
</tr>
<tr>
<td>DTAC</td>
<td>Dodecyl trimethyl ammonium chloride</td>
</tr>
<tr>
<td>DS⁻</td>
<td>Dodecyl sulfate anion</td>
</tr>
<tr>
<td>Eq.</td>
<td>Equation</td>
</tr>
<tr>
<td>Fig.</td>
<td>Figure</td>
</tr>
<tr>
<td>GDS</td>
<td>Gibbs dividing surface</td>
</tr>
<tr>
<td>GHF</td>
<td>Gas hydrate formation</td>
</tr>
<tr>
<td>GHs</td>
<td>Gas hydrates</td>
</tr>
<tr>
<td>HBGS&amp;T</td>
<td>Hydrate-based gas storage and transportation</td>
</tr>
<tr>
<td>HBGS</td>
<td>Hydrate-based gas separation</td>
</tr>
<tr>
<td>HP</td>
<td>Hypothesis</td>
</tr>
<tr>
<td>IGE</td>
<td>Interfacial gas enrichment</td>
</tr>
<tr>
<td>KHI s</td>
<td>Kinetic hydrate inhibitors</td>
</tr>
<tr>
<td>LDHIs</td>
<td>Low dosage hydrate inhibitors</td>
</tr>
<tr>
<td>MD</td>
<td>Molecular dynamics</td>
</tr>
<tr>
<td>mM</td>
<td>Millimolar</td>
</tr>
<tr>
<td>NGHs</td>
<td>Natural gas hydrates</td>
</tr>
<tr>
<td>PVP</td>
<td>Polyvinylpyrrolidone</td>
</tr>
<tr>
<td>PVCap</td>
<td>Polyvinylcaprolactam</td>
</tr>
<tr>
<td>RQ</td>
<td>Research question</td>
</tr>
<tr>
<td>sI</td>
<td>Structure I</td>
</tr>
<tr>
<td>sII</td>
<td>Structure II</td>
</tr>
<tr>
<td>sH</td>
<td>Structure H</td>
</tr>
<tr>
<td>SDS</td>
<td>Sodium dodecyl sulfate</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>--------------------------------------------</td>
</tr>
<tr>
<td>SFG</td>
<td>Sum frequency generation</td>
</tr>
<tr>
<td>SHS</td>
<td>Sodium hexadecyl sulfate</td>
</tr>
<tr>
<td>STS</td>
<td>Sodium tetradecyl sulfate</td>
</tr>
<tr>
<td>TBAB</td>
<td>Tetra-butyl ammonium bromide</td>
</tr>
<tr>
<td>TBA⁺</td>
<td>Tetra-butyl ammonium cation</td>
</tr>
<tr>
<td>TEAB</td>
<td>Tetra-ethyl ammonium bromide</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>TMAB</td>
<td>Tetra-methyl ammonium bromide</td>
</tr>
<tr>
<td>TPeAB</td>
<td>Tetra-pentyl ammonium bromide</td>
</tr>
<tr>
<td>TPrAB</td>
<td>Tetra-propyl ammonium bromide</td>
</tr>
<tr>
<td>wt.</td>
<td>weight</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

This fast-growing world is putting pressure on human-beings to cope with the surge in energy demand while having to sustain the environment. As a result, an enormous body of scientific research has been undertaken to seek new energy sources and establish viable technologies for mitigating greenhouse gas emissions. Since world energy is forecasted to continue relying on fossil fuels, it leads to serious concerns about the severe environmental impacts of carbon dioxide emissions as well as the ongoing depletion of conventional fuel reserves. Amid such challenging context, gas hydrates (GHs) have emerged as opening up new gateways to tackling the energetic and environmental issues. For example, the abundance of natural gas hydrates (NGHs) throughout global ocean sediments and permafrost regions provides immense amounts of low-carbon unconventional fossil fuels. Meanwhile, synthetic gas hydrates open a novel approach for the capture and sequestration of anthropogenic carbon dioxide. Moreover, GHs also play an important role in a number of other sectors related to safety, environment and production such as flow assurance, gas storage and transportation, gas separation and desalination.

Despite such immense potential of application, the utilization of gas hydrates strictly requires the ability of controlling their kinetics of formation and dissociation. The manipulation of hydrate formation kinetics can be implemented through the addition of appropriate additives to the hydrate formation medium. As such, intensive research activities have been undertaken to investigate the effects of different additives on gas hydrate formation and search for new additives with a better performance. Previous works, however, focused primarily on macroscopic measurements and descriptions while the fundamentals underlying the experimental observations remain poorly understood. In other words, there is a substantial gap in knowledge about the molecular mechanisms behind of the influences of additives on gas hydrate formation.

This PhD research aims to gain new molecular insights into the effects of additives on gas hydrate formation. The influence of important additives such as surfactants, hydrophobic solid surfaces and inorganic ions on gas hydrate formation are subjected to study at molecular levels. The utilization of a wide range of research techniques (including hydrate kinetics measurements, in situ visual observation, surface-susceptible vibrational spectroscopy, bulk-specific vibrational spectroscopy and molecular dynamics simulation) makes it possible to unravel the molecular picture behind the hydrate kinetics data. Specially, the primary aim is to uncover the intrinsic
relation between the additive-induced change in local water structure and gas hydrate formation. For example, the roles of the interfacial water alignment, hydrophobic hydration, hydrophobic effect, and ion-specific effect on gas hydrate formation are of particular interest. The thesis ends up with a hypothesis of hydrophobic effect on gas hydrate formation in the presence of additives which can serve as a universal explanation for various effects of additives on gas hydrate formation. With significant fundamental knowledge gained, this research provides steps toward mastering the design and use of additives to manipulate gas hydrate kinetics and ultimately contributes to the establishment of gas hydrates-based technology for tackling industrial and environmental issues.

The remaining content of this thesis is organized as follows:

Chapter 2: Literature Review. This chapter presents a review of the literature and identifies the gaps in knowledge.

Chapter 3: Research Objectives and Hypotheses. This chapter presents research questions, hypotheses to address the research questions and the research designs to test the hypotheses.

Chapter 4: Experimental Apparatus and Computational Methods. The experimental setup and the computational methods are described in this chapter.

Chapter 5: Unexpected Inhibition of CO₂ Hydrate Formation in Dilute TBAB Solution and the Critical Role of Interfacial Water Structure. This chapter provides the new findings about the unexpected dual effects of tetra-butyl ammonium bromide on CO₂ hydrate formation and the critical role of the interfacial water structure in governing gas hydrate formation.

Chapter 6: Inhibition of Methane Hydrate Formation by Water Alignment underneath Surface Adsorption of Surfactants. This chapter presents novel findings about the dual effects of sodium dodecyl sulfates on methane gas hydrate formation and provides an insightful discussion about the physics underlying the effects of surfactants on gas hydrate formation.

Chapter 7: Interfacial Gas Enrichment at Hydrophobic Surfaces and the Origin of Gas Hydrate Formation by Hydrophobic Solid Particles. This chapter provides molecular new insights into the mechanism of the promotion of gas hydrate formation by hydrophobic solid particles (including dry water).

Chapter 8: The Dual Effect of Sodium Halides on the Formation of Methane Hydrate. This chapter presents the extraordinary findings about the hydrate promotion by halide ions and provides a deep
discussion about the possible mechanism of this peculiar phenomenon based on the ion-specific theory.

Chapter 9: Hydrophobic Effect on Gas Hydrate Formation in the Presence of Additives. This chapter incorporates all the new findings from previous chapters and in the literature, from which a new hypothesis of hydrophobic effect on gas hydrate formation is proposed. This hypothesis can serve as a universal explanation for the various effects of additives on gas hydrate formation.

Chapter 10: Conclusions and Remarks

Appendix
Chapter 2

Literature Review

2.1 Gas clathrate hydrates

Gas hydrates (or clathrate hydrates) are ice-like crystalline solids comprising water and suitable gases. The water molecules (the host) form a cage-like hydrogen bonded structure which physically encapsulates the gas molecules (the guest) inside, and the encaged gas molecules, in turn, exert a multi-directional force to prevent the cage-like structure from collapsing [1, 2]. Such host-guest cooperative interaction makes gas hydrates more thermodynamically stable than ice (i.e. at a given pressure, gas hydrates can form at a temperature well above freezing point of water).

Like other crystalline solids, gas hydrates are constructed from the unit cells. Depending on the size and sometimes the composition of the guest, the resulting gas hydrate can have one of three types of unit cells as shown on Figure 2.1 [2, 3]. The corresponding hydrate structures are termed as structure I (sI), structure II (sII) and structure H (sH), respectively [2, 3]. In structure I, the unit cell is a body-centered cubic lattice constituted by two small cages and six large cages. The small cage is a pentagonal dodecahedron and has a notation of $5_{12}$ which indicates that the cage has twelve pentagonal faces. The large cage is a tetra-decahedron (14-faced) and has a notation of $5_{12}6_2$. This notation means that each large cage consists of twelve pentagonal faces and two hexagonal faces. In an ideal combination, each cage (small and large) contains one gas molecule (i.e. CH$_4$ or CO$_2$). This means there are eight gas molecules being encaged in one unit cell of sI. Since the cages share their vertices and faces with others, only 46 water molecules are needed to form eight cages in the unit cell of sI. Hence, each sI unit cell comprises eight gas molecules and 46 water molecules, resulting in the ideal composition being $X.5.75H_2O$ where $X$ denotes the gas (e.g. CO$_2$, CH$_4$, etc.) and $n = 5.75$ is the ratio between the number of water molecules and the number of gas molecules. This ratio is also referred to as the hydration number. However, gas hydrates are non-stoichiometric inclusion compounds and, thus, the hydration number varies considerably depending on the hydrate former (the guest) and the forming condition. Methane occupies about 95% of the large cages and 85% of the small cages, giving $n \approx 6.0$ [4]. Carbon dioxide can only occupy 50% of the small cage, giving $n \approx 6.6$ while ethane is practically too large to fit the small cages, giving $n \approx 7.9$ [5, 6]. The reciprocal value of $n$ is a measure of gas storage capacity of the hydrate, which has important implications in the applications.
The unit cell of structure II is a face-centered cubic lattice which comprises 16 small cages ($5^{12}$) and eight large cages ($5^{12}6^4$) [5]. The notation $5^{12}6^4$ indicates that the large cage is a hexakaidecahedron with twelve pentagonal (5-sided) faces and four hexagonal (6-sided) faces. The sII large cage is larger than the sI large cage so sII structure can fit bigger guests such as propane, iso-butane and so on. Each sII unit cell is composed of 136 water molecules and 24 guest molecules in the full occupancy configuration, resulting in an ideal hydration number being $n = 136/24 = 5.67$. However, the practical hydration number is larger due to incompleteness of cage occupancy.

Structure H is less common compared to structure I and structure II. Its unit cell is more complex than those of sI and sII as the unit cell is composed of three types of cages [three small cages ($5^{12}$), two medium cages ($4^35^66^3$) and one large cage ($5^{12}6^8$)]. The notations of the cages are self-explained, similar to those in sI and sII above. To form sH clathrate hydrates, it needs a big guest such as cyclo-heptane to fill the large cage and a small “help guest” such as methane to fit the small and medium cages [3]. While the big guest cannot occupy the small and medium cages, these cages still need to be filled by a small guest to make the whole structure stable. Because of this reason, the small guest is called “help guest”.

**Figure 2.1** The constitution of three common structures of gas hydrates [3]. Depending on the sizes and compositions of the guests, the resulting clathrate can have one of three crystal structure as indicated. The most common hydrate formers of each structure are also shown.

Despite such astounding simplicity of their chemical composition, gas hydrates have been a topic of enduring interest. Since first discovered in 1810 by Sir Humphrey Davy [1], clathrate hydrates have increasingly attracted a widespread attention of researchers. Even though, over the subsequent century, gas hydrate research was merely for the satisfaction of laboratory curiosity. Only from 1934 when Hammerschmidt [7] confirmed that clathrate hydrates are responsible for
subsea pipelines plugging, these inclusion compounds were considered as a nuisance to flow assurance [2, 3, 8]. Indeed, the finding of Hammerschmidt sparked a flourishing growth in hydrate research, with a primary goal being for the prevention of hydrate formation inside transmission lines. From the late of 20th century, many promising applications of gas hydrates started to be conceptualised and demonstrated, including gas storage and transport [9-12], gas separation [13-16], sequestration of anthropogenic \( \text{CO}_2 \) [17-22] and many more. Such new perspective on clathrate hydrates has further drawn the attention of academia into this field. Also, the research started to focus on gas hydrate promotion, in parallel with the pre-existing hydrate inhibition direction. Nowadays, gas hydrates become an applied science with dynamic growth in the number of scientific publications and form dedicated themes in many scientific journals.

2.2 The formation of gas hydrates

2.2.1 Macroscopic description and molecular concepts

Gas hydrates form spontaneously when water contacts the gas under elevated pressure and low temperature [2, 3]. Figure 2.2 shows a typical T-P graph (T: temperature, P: pressure) recorded from an isochoric hydrate reactor. The first drops in both T and P at the beginning of experiments are due to the initial cooling of the system. The sharp rise in T coupled with a huge drop in P indicates the onset of the exothermic formation of gas hydrate inside the reactor. The awaiting period between the point of time when T&P fall into hydrate-forming condition and the onset of hydrate formation is described as the induction time. At microscopic scale, it is the time needed for the gas to dissolve into water to produce a supersaturated solution and for the water structure to rearrange itself to accommodate the gas and form initial hydrate crystals. This graph is said to be typical because from its T-P profiles, different stages happening in gas hydrate formation process can be identified clearly.

In nature, gas hydrates form naturally in the locations where the forming condition is met such as in permafrost regions or marine sediments with a water depth of between hundreds and thousands meters [23]. The temperature and hydrostatic pressure in those locations fall into gas hydrate stability zone which sustains the enclathration of natural gas by marine water. Interestingly, \( \text{CO}_2 \) hydrate formed rapidly when liquid \( \text{CO}_2 \) was disposed directly onto ocean floor at a water depth of 3650 m [24]. This experimental observation supports the idea of sequestration of \( \text{CO}_2 \) in subsea locations [18, 25].
Figure 2.2 A typical T-P graph showing different stages involved in gas hydrate formation process.

The guest used was methane. The experiment was conducted in an isochoric reactor at initial pressure of 7.5 MPa and target temperature set to 0.5°C.

Despite such clear macroscopic observations, the molecular picture of gas hydrate formation remains poorly understood. Especially, the time-dependent (kinetic) properties are the most challenging domain in gas hydrate research [26, 27]. To date, the molecular mechanism of gas enclathration still remains controversial [1, 28-30]. Amongst few hypotheses available in the literature [1, 28-30], the labile clusters theory [1, 28] probably provides the most insightful description of the formation mechanism. This theory was developed by Sloan et al. based on a classical “iceberg” model originally proposed by Frank and Evans [1]. It considers gas hydrate nucleation initiating from building locally structured water clusters around individual dissolved gas molecules (known as labile clusters or hydrophobic hydration shells). Under hydrate-forming condition, the hydration shells transform into gas hydrate cages. Then, the cages agglomerate into hydrate nuclei via face-sharing. When the nucleus size exceeds a critical value, the nuclei grow rapidly into big hydrate masses (Figure 2.3) [1].

Significant research efforts based on experimental measurements [31-33] and computer simulations [34-36] have sought the evidence of labile clusters. Majority of the outcomes support the existence of a local water structure (hydration shell) around a dissolved guest, in particular, a methane molecule. Even though, the results indicate that the number of water molecules on a hydration shell of methane (the coordination number) is around 19 [33, 37], which is smaller than the desired values of 20 for small sI (5^{12}) and 24 for large sI (5^{12}6^{2}) cages. Hence, the hydration shells must undergo structural transformation, by adopting water molecules from the bulk, through various intermediate states before accomplishing a correct conformation of clathrate hydrate. The
time needed for such structural transformation is apparently manifested by the induction period in gas hydrate experiments.

**Figure 2.3** Mechanism of gas hydrate formation through labile clusters hypothesis as reproduced from Sloan et al [1]. Different stages of gas enclathration process are explained in the figure.

2.2.2 *The formation of gas hydrate at the interface*

Gas hydrate formation normally initiates at the gas-water interface rather than in the bulk liquid [27]. This characteristic is highly important. It suggests that interface-active agents may affect hydrate formation more effectively than bulk-active ones do. It also infers that the interfacial water needs to be accounted for when explaining gas hydrate phenomena. The interfacial formation of gas hydrates is evidenced by the occurrence of a hydrate thin film at the guest-water interface (in quiescent condition) [38-40]. The film stops growing in its thickness when it becomes diffusion-resistant and thereby hinders the mass transfer across the interface [38]. For example, the final thickness of methane hydrate film was reported to be in between 20-100 μm depending on experimental condition [38]. The formation of hydrate film was more observable in the system containing a small water droplet placed in a guest phase or a small guest bubble placed in an aqueous phase [39-41]. Figure 2.4 shows the occurrence of a methane hydrate film at the surface of a water droplet in methane environment [41].
Figure 2.4 The formation of a methane hydrate thin film at a methane-water interface [41]. The initiation and propagation of a thin hydrate film on droplet’s surface is clearly shown.

Figure 2.5 Explains the mechanism of hydrate formation at a methane-water interface, for example [42]. First, CH$_4$ molecules transfer across the interface into water. Then the interfacial water forms hydrate cages around dissolved CH$_4$ molecules right under the interfacial plane. Finally, the cages agglomerate into a hydrate crystal. The resulting hydrate crystal then obstructs the dissolution of methane into water. Consequently, no further hydrate growth can take place under the interface. Therefore, only a hydrate film is formed. In contrast to the quiescent system, in an agitated system, the turbulence breaks the film and the convection flow conveys the hydrate nuclei into the bulk where they grows into big hydrate masses [1]. As such, rapid growth of hydrate masses in the bulk phase of an agitated system is possible.

Figure 2.5 Methane hydrate formation at methane-water interface [42]. Three proposed steps are indicated in the figure.

2.3 The significance of gas hydrates

Despite the simplicity of their chemistry, gas hydrates are known to be a fascinating science and immense potential of applications/implications in many sectors. Figure 2.6 outlines the fields on which gas hydrates have the most impacts. As it is presented on the figure, gas hydrates poses both tremendous opportunities of applications as well as big challenges to industrial production and environmental protection. The sections below provide more details about these areas.
2.3.1 Gas hydrates in energy sector

Gas hydrates play an important role in the energy industry in both terms of providing opportunities and posing challenges to this sector. In the aspect of opportunities, natural gas hydrates (NGHs) have been shown to be excellent sources of unconventional fuels. The energy amount contained in NGHs is estimated to be double of the total energy from conventional fossil fuels available [3, 5]. Moreover, NGHs are classified as a clean fuel owing to their relatively low carbon content compared to coals and oils. Due to such outstanding advantages, NGHs are an attractive alternative energy source, especially amid the ongoing depletion of conventional fossil fuels being foreseeable.

Another promising application of gas hydrates in energy sector is the storage and transport of fuel gases in the form of their hydrates. Hydrate-based gas storage and transportation (HBGS&T) is considered to be a novel technology [9-12] because theoretical calculation shows that 1 m$^3$ of gas hydrate can store as much as 180 m$^3$ of natural gas (measured at the standard condition) [5]. In practice, a storage capacity of 175 m$^3$ of methane per 1 m$^3$ of hydrate has been reported [9]. Moreover, HBGS&T is safer than the traditional liquefaction technology because the conversion of

---

**Figure 2.6** The applications/implications of gas hydrates to industrial productions and the environment
gas hydrate into fuel gas is highly controllable. As a result, the risk associated with physical explosion during handling can be eliminated.

However, in the aspect of posing challenges, the undesired formation of gas hydrates inside subsea pipelines causes a long-standing problem for flow assurance [2, 3]. The resulting hydrate builds up its mass, obstructs the flow and eventually blocks the transmission lines [5, 7]. This problem was first discovered in 1934 by Hammerschmidt [7] and still remains to be the biggest nuisance to flow assurance. For example, the catastrophic explosion of BP’s oil rig in the Gulf of Mexico in 2010 was attributed to gas hydrates [5]. Consequently, the inhibition of gas hydrate formation still remains to be an active and attractive domain of gas hydrate research.

2.3.2 Gas hydrates and the environment

Gas hydrates have a strong link to the atmospheric and oceanic environment [43, 44]. They can have both positive and negative impacts on the sustainability of the Earth’s climate. On one hand, CO$_2$ hydrate can provide a safe and long-term sequestration of anthropogenic carbon dioxide in geological reservoirs [17, 18]. Thanks to the formation of CO$_2$ gas hydrates, the sequestered CO$_2$ is immobilised in its clathrate lattice which prevents it from returning to the atmosphere [17-20]. Especially, with the observation of a rapid formation of CO$_2$ gas hydrate from liquid CO$_2$ on ocean floor of 3700 m depth [24], the idea of carbon sequestration via direct subsea disposal of liquid CO$_2$ has gained significant interest of researchers [19, 21, 22]. On the other hand, natural gas hydrates (NGHs) pose a notable threat to the Earth’s climate. This is because natural gas is a highly active greenhouse gas. The massive occurrence of NGHs throughout the globe is seen not only as an excellent energy source but also as environmental hazard because of the potential risk of catastrophic CH$_4$ release.

2.3.3 Gas hydrates for industrial productions

In the last several decades, a number of potential applications of gas hydrate have been conceptualised and tested. One of the most promising applications is the use of gas hydrate formation /dissociation for the separation and purification of gases, which is commonly referred to as hydrate-based gas separation (HBGS). This is a novel idea and has been investigated intensively during the last decade. The outcome from previous works shows an optimistic perspective on the capability of HBGS for capturing carbon dioxide from flue gases or syngas for CO$_2$ sequestration purposes [13, 14, 45-49]. The principle of this method is quite simple which is based on the selective formation of CO$_2$ gas hydrate over the other components in the gas mixtures, which is depicted on Figure 2.7 for example of capturing CO$_2$ from flue gas. The process consists of two
stages corresponding to the formation and dissociation of CO$_2$ gas hydrate, respectively. In the first stage, carbon dioxide is separated from gas mixture by its hydrate formation. Then the CO$_2$ hydrate is conveyed to another stage in which it is dissociated to produce a high-purity CO$_2$ stream for subsequent sequestration and a spent fluid which is recycled to the formation stages.

![Diagram of gas separation process](image)

**Figure 2.7** Hydrate-based gas separation for the capture of CO$_2$ from flue gas. The selective formation of CO$_2$ hydrate separates this gas from the mixture. Then the dissociation of CO$_2$ hydrate in the next stage produces CO$_2$ stream and spent water. The spent water is recycled to hydrate formation stage.

### 2.4 The effects of additives on gas hydrate formation

The formation of gas hydrates is very sensitive to the impurity of the medium. The presence of any foreign entities other than water and the guest can cause substantial effects on thermodynamic and kinetic properties of the gas hydrate system. The foreign entities (additives) may be intentionally added to affect the formation kinetics, or they may present in hydrate systems naturally such as dissolved salts, bio-surfactants and colloids. In this section, I review the effects of important additives on gas hydrate formation and discuss the existing explanations for their effects.

#### 2.4.1 The effects of thermodynamic inhibitors

Thermodynamic hydrate inhibitors (THIs) are the additives that shift the phase equilibrium of a hydrate system to lower temperature and higher pressure, thereby, inhibiting the formation of gas hydrates in a prevailing condition. Systematic investigations into hydrate inhibitors were triggered in 1934 when Hammerschmidt [7] confirmed that clathrate hydrates are responsible for subsea pipeline plugging. The best known THIs are alcoholic compounds (e.g., methanol, ethylene glycol, etc.) and inorganic salts [8, 50, 51]. Since THIs affect the bulk phase of hydrate system, they need high dosages (30-50 mass %) to give a satisfactory inhibition performance [51-53]. Such high dosages lead to serious concerns about the operational and environmental costs [51-53].
Fundamentally, it is widely agreed that THIs inhibit gas hydrate formation by decreasing the activity of water. They are highly polar molecules (or ions in the case of salts) which bind water strongly by hydrogen bonds (or by electrostatic forces for ions). The strong binding leads to an increased competition with the hydrate former for water. Consequently, there is less water available for forming hydrate with the gas [1]. The effectiveness of a THI depends upon its capability of binding water [50]. For example, ethanol and ethylene glycol have similar molar volumes but ethylene glycol has two hydroxyl groups available for hydrogen bonds while ethanol has only one. Consequently, ethylene glycol gives a better hydrate inhibition than ethanol does [50]. Similarly, multivalent ions bind water more strongly than large-size monovalent ions do [54]. As a result, multivalent ions are better THIs compared to large-size monovalent ions.

However, a number of THIs also exhibit as hydrate promoters when they are used at low concentration. For example, experiments have reported a promoted methane hydrate formation in dilute alcoholic solutions [1, 55, 56]. The fundamentals underpinning such promoted hydrate formation in the dilute solutions of THIs cannot be explained by the available literature.

2.4.2 The effects of low-dosage hydrate inhibitors on gas hydrate formation

Unlike THIs which affect the bulk phase of hydrate-forming systems, low-dosage hydrate inhibitors (LDHIs) are interface-active agents which influence the interfacial properties of gas hydrates. The use of LDHIs is of increasing interest owing to their low operational dosages, typically less than 1 mass % [52, 53]. LDHIs are conventionally categorised into kinetic hydrate inhibitors (KHIIs) and anti-agglomerants (AAs) which are different from each other by the acting mechanisms. While KHIIs act primarily as gas hydrate anti-nucleators, AAs allow gas hydrates to form, but prevent hydrate nuclei from further agglomerating into big hydrate masses [52]. The classical KHIIs are vinylic polymers, of which, polyvinylpyrrolidone (PVP), polyvinylcaprolactam (PVCap) and antifreeze proteins (AFPs) are the most popular [8, 57]. AAs are surface-active compounds such as alkyl aromatic sulphonates or alkylphenyethoxylates [53]. Beside these traditional LDHIs, a vast number of new LDHIs are being introduced. Some of them are listed in Table 2.1.

It is proposed that LDHIs inhibit gas hydrate formation by binding to the surface of an ensuing hydrate nuclei [58]. The adsorption of LDHIs molecules on the surfaces of hydrate nuclei disrupts the growth of hydrate crystals [58]. However, recent studies have shown that an accelerated hydrate growth can occur in the presence of LDHIs [59-61]. For example, it was found that while 0.5 and 1.5 mass% of PVCap could suppress the nucleation and growth rate of gas hydrates
efficiently, 3.0 mass % of this agent induced a catastrophic hydrate growth [60]. In general, the presence of LDHIs can retard the nucleation and growth of gas hydrates within a certain period after which a fast growth takes place steadily [59, 60, 62]. The reason for such catastrophic hydrate growth is not clear [59]. Therefore, further fundamental investigations into this phenomenon are needed.

Table 2.1 Unconventional low dosage hydrate inhibitors of increasing interest

<table>
<thead>
<tr>
<th>LDHIs</th>
<th>The predominant effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pectin</td>
<td>66% reduction of working dosage and 10-fold increase in effective time in comparison with typical KHI [63]</td>
</tr>
<tr>
<td>Amino acids</td>
<td>Good inhibition capacity and environmental friendliness [64-66]</td>
</tr>
<tr>
<td>Poly-carbonyl amides</td>
<td>Effective LDHIs [67, 68]. Much better inhibition achieved when combined with nonylphenol ethoxylates or poly ethylene glycol [69]</td>
</tr>
<tr>
<td>Ionic liquids</td>
<td>Good inhibition capacity [70, 71]</td>
</tr>
<tr>
<td>Natural products (NPs)</td>
<td>NPs such as chitosan [72] and starches [73] are promising green LDHIs.</td>
</tr>
<tr>
<td>Synergists</td>
<td>The addition of a synergist (such as L-tyrosine [74], poly ethylene oxide [75], NaCl [76], ionic liquids [71] and so on) enhances the inhibition performance of the used LDHIs</td>
</tr>
</tbody>
</table>

2.4.3 Surfactants effects on gas hydrate formation

2.4.3.1 Physicochemical characteristics of surfactants

Surfactants are amphiphilic compounds. Each surfactant molecule consists of a hydrophilic (water-liking) head and a hydrophobic (water-hating) hydrocarbon tail (as shown on Figure 2.8a for sodium dodecyl sulfate). Due to such special molecular structure, surfactants have a tendency of minimising the exposure of the hydrophobic tails to aqueous phase [77]. As such, surfactants prefer adsorbing on the hydrophobic-aqueous interface with hydrophilic heads remaining in the solution and hydrophobic tails spreading into the hydrophobic phase (Figure 2.8b). Otherwise, when the interfacial adsorption is saturated, they aggregate to form micelles in solutions (Figure 2.8b). The micellization takes place only when the concentration of the surfactant is higher than a certain value called critical micellar concentration (CMC) and the solution temperature is above a certain value called Krafft point (Figure 2.8c). Both CMC and Krafft point are specific to each surfactant [78].
The presence of surfactants in a solution induces substantial changes in physicochemical properties of the system. Interfacial adsorption of surfactants decreases the interfacial tension between the solution and the adjacent phase [79] which may affect the mass transfer across the interface. It may also carry charge to the interface and subsequently influence the orientation and mobility of interfacial water [80, 81]. The presence of surfactants increases the solubility of gases in aqueous solutions [82-84]. Moreover, due to its amphiphilic nature, a surfactant molecule produces two opposite effects on the local water structure. The hydrophobic tail organises surrounding water molecules into a clathrate-like cluster, as postulated by Frank and Evans in their well-known work in 1945 [85]. The hydrophilic head (together the counter ion in the case of ionic surfactant) binds water strongly and disrupts the local water structure, similar to the effect of inorganic salts [86]. These special properties are of great relevance to gas hydrate formation.

2.4.3.2 Evidence of surfactants affecting gas hydrate formation

Surfactants probably provide the best acceleration of gas hydrate kinetics. It was reported that sodium dodecyl sulfate (SDS) solution of 284 ppm increased the rate of methane enclathration by 700 times [87]. This surfactant was also investigated intensively in many other works [88-92]. Besides SDS, a huge number of other surfactants were subjected to investigations. The most common of them are listed on Table 2.2. In general, it was found that the addition of surfactants could increase hydrate kinetics by the orders of magnitude. Regarding the effect of surfactant types, it was sometimes noted that anionic surfactants were more effective than non-ionic surfactants yet
cationic surfactants were effective only at low concentrations [93]. However, this conclusion might be overgeneralized as dodecyl amine hydrochloride (DAH) and N-dodecylpropane-1,3-diamine hydrochloride (DN2Cl), both are cationic, exhibited a strong promotion of methane hydrate formation at a concentration as high as 3000 ppm [94]. Interestingly, some surfactants display better promotion performances when are mixed. For example, a more efficient promotion was achieved when SDS was mixed with tetrahydrofuran (THF) [88, 90]. Likewise, tetra-butyl ammonium bromide (TBAB) and dodecyl trimethyl ammonium chloride (DTAC) displayed a better promotion under a shared effect than the individual effect of each surfactant [45].

Table 2.2 Surfactants that are widely used in clathrate hydrate research

<table>
<thead>
<tr>
<th>Type of surfactants</th>
<th>Name of surfactants</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anionic surfactants</td>
<td>Sodium dodecyl sulfate (SDS)</td>
<td>[88-92, 95]</td>
</tr>
<tr>
<td></td>
<td>Sodium tetradecyl sulfate (STS)</td>
<td>[95]</td>
</tr>
<tr>
<td></td>
<td>Sodium hexadecyl sulfate (SHS)</td>
<td>[95]</td>
</tr>
<tr>
<td></td>
<td>Sodium oleate</td>
<td>[95]</td>
</tr>
<tr>
<td>Cationic surfactants</td>
<td>Tetra-n-butyl ammonium bromide (TBAB)</td>
<td>[14, 16, 45, 96-98]</td>
</tr>
<tr>
<td></td>
<td>Dodecyl trimethyl ammonium chloride (DTAC)</td>
<td>[45]</td>
</tr>
<tr>
<td></td>
<td>Dodecyl amine hydrochloride (DAH)</td>
<td>[94]</td>
</tr>
<tr>
<td></td>
<td>N-dodecylpropane-1,3-diamine hydrochloride (DN2Cl)</td>
<td>[94]</td>
</tr>
<tr>
<td>Non-ionic surfactants</td>
<td>Tetrahydrofuran (THF)</td>
<td>[13, 88, 90, 91]</td>
</tr>
<tr>
<td></td>
<td>Ethoxilated nonylphenol</td>
<td>[99]</td>
</tr>
<tr>
<td></td>
<td>Tween 80</td>
<td>[100]</td>
</tr>
<tr>
<td></td>
<td>Cyclopentane</td>
<td>[101, 102]</td>
</tr>
</tbody>
</table>

2.4.3.3 Governing mechanism of surfactants for gas hydrate formation

The actual mechanism by which surfactants affect gas hydrate formation is poorly understood. There are a number of hypotheses for explaining the accelerated formation of gas
hydrates in surfactant solutions but they are constructed based on assumptions rather than experimental evidence. For example, it is widely believed that surfactant aggregates (micelles) are responsible for the promoted formation of gas hydrates in surfactant solutions [87]. The micelles are deemed to act as minute gas reservoirs which facilitate the gas dissolution and provide nucleation sites for gas hydrate formation [87]. However, this hypothesis has been under a criticism that surfactants, more likely, cannot form micelles in the condition of gas hydrate experiments since the working temperature goes lower than the Krafft point [92, 103]. Even though micelles are still used as a theoretical framework for interpreting the accelerated formation of gas hydrates in surfactant solutions on these days [104].

![Figure 2.9 Illustration of a SDS surfactant micelle in ethane hydrate-forming system as reproduced from Zhong et al. [87]. The surfactant micelle is thought to act as a minute gas reservoir thereby facilitates the gas hydrate formation. The grey area in the figure indicates the interior space with high density of ethane.](image)

However, given if micelles do present in hydrate-forming systems, how do they promote hydrate formation still being an open question. The micelles are assumed to act as minute gas reservoirs and provide nucleation sites for gas hydrates [87]. Indeed, a hydrophobic guest (i.e. ethane as on Figure 2.9) can be favourably confined in the interior (core) of the micelle thanks to hydrophobic interactions. Therefore, surfactant micelles may act as minute gas reservoirs in the solution. However, the nucleation of hydrate in the confined space within a micelle may not be possible, due to the exclusion of water. Similarly, the nucleation of gas hydrate on or around a micelle is possibly unfavourable as well, due to the high density of ions in such location (as seen on Figure 2.9). The ions cause a radical disruption of local water structure, similar to in concentrated saline solution [86]. Hence, more convincing evidence is needed to confirm or rule out such role of surfactant micelles in gas hydrate formation. In another hypothesis, it was proposed that the
accelerated formation of gas hydrates in surfactant solutions arises from the adsorption of surfactants on hydrate-liquid interfaces [105]. The observed promotion was attributed to the decrease in interfacial tension due to the surfactant adsorption [92, 105].

Table 2.3 Hydrate promotion capability of different surfactants

<table>
<thead>
<tr>
<th>Name of surfactants</th>
<th>Promotion effectiveness</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium dodecyl sulfate (SDS)</td>
<td>Strong</td>
<td>[95]</td>
</tr>
<tr>
<td>Sodium tetradecyl sulfate (STS)</td>
<td>Strong</td>
<td></td>
</tr>
<tr>
<td>Sodium hexadecyl sulfate (SHS)</td>
<td>Moderate</td>
<td></td>
</tr>
<tr>
<td>Sodium oleate (SO)</td>
<td>Indiscernible</td>
<td></td>
</tr>
<tr>
<td>Sodium dodecyl sulfate (SDS)</td>
<td>Strong</td>
<td>[94]</td>
</tr>
<tr>
<td>Dodecyl trimethyl ammonium chloride (DTAC)</td>
<td>Indiscernible</td>
<td></td>
</tr>
<tr>
<td>Dodecyl amine hydrochloride (DAH)</td>
<td>Strong</td>
<td></td>
</tr>
<tr>
<td>N-dodecylpropane-1,3-diamine hydrochloride (DN2Cl)</td>
<td>Moderate</td>
<td></td>
</tr>
</tbody>
</table>

Nonetheless, the available hypotheses cannot provide satisfactory explanation for the dual effects (both promotion and inhibition) of a given surfactant [106]. It is also hard to explain the difference in the effectiveness between surfactants. Table 2.3 shows that the effectiveness of different surfactants is various. For example, Du et al. compared the effects of four surfactants on methane hydrate formation in the same experimental condition [94]. The results showed that sodium dodecyl sulfate has the strongest effect (in term of decreasing induction time and increasing methane uptake), followed by dodecyl amine hydrochloride and then N-dodecylpropane-1,3-diamine hydrochloride. The forth surfactant, dodecyl trimethyl ammonium chloride, however, has no discernible effect of methane hydrate kinetics [94]. Similarly, Okutani et al. showed that sodium dodecyl sulfate and sodium tetradecyl sulfate enhance gas hydrate kinetics strongly while the effect of sodium hexadecyl sulfate is lesser [95]. In the contrast, sodium oleate has no discernible effect [95]. The available literature is insufficient for explaining these experimental data.
2.4.4 The effects of hydrophobic particles on gas hydrate formation

2.4.4.1 The hydrophobicity of solid surfaces

The term hydrophobicity describes the water-hating characteristics of material. It is macroscopically measured by the non-wettability of a surface. The counter term is hydrophilicity which indicates the wettability of a surface. Quantitatively, the contact angle of a water droplet on a surface is a measure of surface hydrophobicity (Figure 2.10). In gas hydrate formation, the involvement of solid surfaces is inevitable. There always present the surface of equipment. Likewise, the formation of natural gas hydrates in geological sediments is always affected by the surfaces of minerals, rocks and solid masses. In many cases, solid particles are intentionally added to hydrate-forming systems as hydrate additives, amongst them hydrophobic fumed silica powder is the best known. This powder is of ultrafine size with the surface being coated by alkyl chains [107]. In gas hydrate experiments, it is mixed with water to a proportion of 1-5 mass % by using a high-speed blender to disperse water phase into minuscule droplets whose surfaces are fully covered by the powder [9, 10, 108]. The resulting mixture is apparently dry, free-blowing and usually referred to as dry water [9, 10].

![Figure 2.10 Contact angle as a measure of hydrophobicity of a solid surface](image)

2.4.4.2 Evidence of hydrophobic particles affecting gas hydrate formation

Previous studies showed that hydrophobic particles (or more strictly saying, hydrophobic solid surfaces) can promote the formation of gas hydrates effectively. Especially, dry water produces an excellent promotion for both carbon dioxide [109] and methane [9, 10, 110] hydrates. For example, the methane uptake was increased from 3 (v/v, gas volume in standard condition per hydrate volume) in ordinary water to 175 (v/v) in dry water, under the same experimental condition [9]. The induction time was also shortened to 5-10 minutes in dry water system [9]. In another work, the effect of surface hydrophobicity of sands on hydrate formation was studied [111]. The results showed a decrease in the induction time, from 576 s for untreated (hydrophilic) sands to 71 s for treated (hydrophobic) sands [111]. Furthermore, hydrate formation was more deterministic (less stochastic) when hydrophobic sands were used [111].
Table 2.4 The most widely used hydrophobic solid surfaces in gas hydrate formation

<table>
<thead>
<tr>
<th>Solid surfaces</th>
<th>Predominant effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrophobic fumed silica (dry water)</td>
<td>Gas uptake increased from 3 (v/v) in ordinary water to 175 (v/v) in dry water with short induction time [9]. No agitation needed [9, 10]</td>
</tr>
<tr>
<td>Hydrophobized silica sands</td>
<td>Induction time decreased from 576 (s) in original (hydrophilic) sand beds to 71 (s) in treated (hydrophobic) sand bed; Induction time was more reproducible in hydrophobic sand beds [111]</td>
</tr>
<tr>
<td>Hydrophobized glass beads</td>
<td>Shortened induction time and increased hydrate formation rate. No agitation needed [112]</td>
</tr>
<tr>
<td>Metallic surfaces</td>
<td>Shortened induction time and enhanced final water conversion [113]</td>
</tr>
<tr>
<td>Wet nanopore activated carbon</td>
<td>Unprecedented high gas uptake (24 g methane per 100 g dry activated carbon) with ultrafast hydrate formation kinetics [11]</td>
</tr>
<tr>
<td>Carbon nanotubes</td>
<td>The gas uptake increased by 300% with shorter induction time compared with pure water [114]</td>
</tr>
<tr>
<td>Graphene oxide</td>
<td>The induction time decreased by 96% compared to the case of pure water [115]</td>
</tr>
</tbody>
</table>

Carbon-based materials also attracted the widespread attention of researchers. For example, methane hydrate formation in confined spaces of activated carbons was studied [11]. The results showed an ultrafast hydrate formation with an unprecedented high methane uptake, namely 24 g CH₄ per 100 g dry activated carbon, achieved under mild condition (2ºC and 3.5 MPa) [11]. Similarly, graphene oxide particles [115] and multi-walled carbon nanotubes [114] were found to provide a good hydrate promotion. Table 2.4 presents a number of common hydrophobic solid surfaces that were used as hydrate promoters. From these data, it suggests that the hydrate formation is possibly governed by the surface hydrophobicity rather than by the chemical nature of the substrates.

2.4.4.3 Governing mechanism of hydrophobic particles for gas hydrate formation

The promoted hydrate formation in the presence of hydrophobic particles is conventionally attributed to the increased interfacial area [9, 11]. For example, the average size of dry water (water droplets covered by hydrophobic silica powder) was found to be 20 μm [9]. Dry water, therefore, is deemed to provide adequate gas-water contact for a fast hydrate formation [9]. Similarly, the
ultrafast methane hydrate formation in activated carbons was attributed to the facilitated methane-water contact in the interior pore surface [11]. In other words, hydrophobic particles are assumed to promote gas hydrate formation through a kinetic route.

However, it was also found that dry water shifted the equilibrium of methane hydrate to higher temperature and lower pressure [108]. This effect indicated that dry water acted as a thermodynamic promoter rather than a phase-contact facilitator. Moreover, hydrate kinetics was improved by increasing the surface hydrophobicity of the solids [111, 116]. These findings are very interesting but they cannot be explained by the available literature.

2.5 The knowledge gaps in the current literature

The literature review and discussion in previous sections have pointed out a significant deficiency of the current literature in understanding the effects of additives on gas hydrate formation. Previous works were overwhelmed on macroscopic measurements of kinetic and thermodynamic properties of hydrate systems under the presence of hydrate additives [117-119] yet insufficient attention was paid to the fundamental understanding. The macroscopic measurements produce experiment-specific results, the results that depend on the conditions adopted (e.g. type and concentration of additives, type of equipment, etc.) [26]. Consequently, it is difficult to generalize and conceptualize the findings.

From the molecular picture of gas hydrate formation, it is factual that water structure plays a vital role in gas hydrates. The formation of gas hydrates is the successive transformation of water structure from initial liquid state to clathrate solid state with intensive breaking and creation of water hydrogen bonds [1, 120]. Therefore, the local structure of liquid water and the dynamics of hydrogen bonds are of paramount importance. The labile cluster, the memory effect and the metastability of hydrate systems are all played by local water structure and hydrogen bonds. However, hydrogen bonds still remain to be a long-standing mystery [121-124]. This knowledge gap has created many difficulties in elucidating hydrate phenomena at the microscopic level, which is apparently reflected by a slow progress in understanding time-dependent properties of gas hydrates (while the structural properties and thermodynamics have been well documented) [26, 27]. It also leads to difficulties in understanding the effects of additives at the molecular level. The existing explanations for the promoted or inhibited hydrate formation in the presence of additives are additive-specific and experiment-specific, meaning that each of the explanations is only valid for a specific experimental condition.
Despite the fact that gas hydrate formation initiates at the interfaces [27, 38-40], the role of interfacial water is neglected in the existing literature. This is a major shortcoming because local water molecules at gas-water interface involve directly in the nucleation of gas hydrates whereby they undergo structural rearrangement and transformation. As such, it is required to know how the additives affect the interfacial water first, before being able to elucidate how such change influences the subsequent formation of gas hydrates. Previous works were unable to quantify the role of interfacial water because the instrumental techniques employed were not interface-specific, and hence, were unable to differentiate the interfacial water from the bulk phase.

In particular, the mechanisms through which additives promote or inhibit gas hydrate formation are controversial and debatable. For example, it is generally agreed that dry water promotes gas hydrate formation kinetically, through increasing interfacial area, which facilitates gas-water contact. However, it was also found that dry water shifted the equilibrium of methane hydrate to higher temperature and lower pressure [108]. This effect indicated that dry water acted as a thermodynamic promoter rather than a phase-contact facilitator. Moreover, hydrate kinetics was improved by increasing the surface hydrophobicity of the solids [111, 116]. These findings are very interesting but they cannot be explained by the available literature.

Similarly, the theories available in the current literature are unable to elucidate the dual (both promoting and inhibiting) effects of a given additive on gas hydrate formation. Experiments have reported that many additives can change from a hydrate inhibitor to a hydrate promoter and vice versa when the working condition is changed. For example, alcohols and inorganic salts are well known thermodynamic hydrate inhibitors (THIs), but the dilute solutions of methanol [1, 55, 56] or sodium halides [125] act as hydrate promoters. The fundamentals underpinning such dual effects are poorly understood. Moreover, it is not known which property of the additive actually governs its effect on gas hydrate formation. The literature reviewed in previous sections has shown that two additives with differences in chemistries, sizes and structures can act analogously on gas hydrate formation whereas many other additives have similar chemistries and structures but act differently (i.e. some surfactants are effective promoters while some others are inactive, see Table 2.3 in Section 2.4.3.3). The available theories/hypotheses fail to explain this observation. In another words, it has not been known what the universal mechanism (of the effects of additives on the formation of gas hydrates) is.


Chapter 3
Research Objectives and Hypotheses

3.1 The objectives of this research

The general objective of this research is to gain new molecular insights into the effects of additives on the formation of gas hydrates. Especially, it aims to provide a universal understanding of the effects of additives on gas hydrate formation which is based on the analysis of the additive-induced changes in the local hydrogen-bonded network of water. Particularly, this research aims to answer following research questions (RQs):

RQ1. How does the change in the interfacial water structure affect the formation of gas hydrates? Given the fact that gas hydrate nucleation takes place at the gas-solution interface, it is important to quantify the role of interfacial water structure in affecting gas hydrate formation. Uncovering such role of interfacial water structure would provide a key gateway to unraveling the molecular mechanism of promotion and inhibition of gas hydrate formation in different conditions.

RQ2. How do surfactants of ultralow concentrations (the concentrations ranging sub-millimolar to millimolar) affect the formation of gas hydrates? The formation of gas hydrates in natural environments occurs in the presence of natural surfactants of ultralow concentrations. However, the effect of ultralow concentrations of surfactants on gas hydrate formation is not reported in the literature. Answering this question is essential and expanding the knowledge of surfactant effects on the formation of gas hydrates.

RQ3. What is the origin of the promotion of gas hydrate formation by hydrophobic solid surfaces (typically dry water)? The mechanism by which hydrophobic solid surfaces (including dry water) promote gas hydrate formation is poorly understood. The answer to this question provides a fundamental picture of the effect of hydrophobic solid surfaces on gas hydrate formation, fulfilling a major knowledge gap in the current literature.

RQ4. What are the factors that determine the effect of ions on gas hydrate formation? Inorganic ions are ubiquitous and they are regarded as thermodynamic hydrate inhibitors. However, the effect of low concentrations of ions on gas hydrate formation is poorly understood. The ion-specific effect on gas hydrate formation has not been well-known. The answer to this question is scientifically and practically necessary.
RQ5. What is the universal mechanism governing the effects of additives on gas hydrate formation? The answer to this question is essential since the available explanations of gas hydrate promotion and inhibition are additive-specific and experiment-specific (each of the explanations is only valid in a specific condition). The answer to this question provides a universal description of the effects of additives on gas hydrate formation and thus fills the major knowledge gap in the current literature.

3.2 Hypotheses and research designs

Followings are the hypotheses (HPs) to address the RQs and research designs to test the HPs.

HP1: Gas hydrate formation is governed by the structure (hydrogen-bonded network) of water at the gas-solution interface. Since the formation of gas hydrates is associated with the rearrangement of water structure at the gas-water interface, if the interfacial water is aligned or bound by an external field, the formation of gas hydrate will be inhibited. This HP answers the RQ1.

HP2: Under ultralow-concentration condition, a surfactant mostly affects interfacial water through surface adsorption at the gas-solution interface while its effect in bulk water can be neglected due to the negligible concentration in the bulk. The surface adsorption of surfactants introduces the charges to the interface and thereby creates an interfacial electrostatic field (IEF). The IEF results in an aligned configuration of water at the gas-solution interface. According to HP1, surfactants solutions of ultralow concentration are inhibitors of gas hydrate formation. This HP answers RQ2.

To validate HP1 and HP2, surfactants solutions of ultralow concentrations are used as the research subject. Two most common surfactants, sodium dodecyl sulfate (SDS) and tetra-butyl ammonium bromide (TBAB), are used. A combination of spectroscopic methods and molecular dynamics simulation are employed to analyse the effect of ultralow concentration of surfactants on the water structure at the interface and in the bulk. In the meantime, hydrate kinetics measurements are carried out to determine the effects of ultralow concentration of surfactants on gas hydrate formation. The kinetics data are correlated with structural data to validate HP1 and HP2. The results are presented in Chapters 5 and 6.

HP3: A hydrophobic solid surface promotes gas hydrate formation through increasing local gas density and the tetrahedral water network near the surface. First, cooperative interactions between a hydrophobic solid surface and dissolved gas molecules can lead to an increased gas
density near the surface. Secondly, the hydrophobic effect leads to an improved tetrahedral network of water near the hydrophobic surface. These two effects accelerate the formation of gas hydrates at hydrophobic-water interface. In contrast, a hydrophilic surface expels gas molecules, resulting in a decreased gas concentration near the surface. Moreover, it binds water molecules strongly and thus disrupts water tetrahedral network near the surface. Consequently a hydrophilic surface inhibits gas hydrate formation. This HP answers RQ3.

To validate HP3, molecular dynamics simulation is employed to analyse local gas density and local water structure near hydrophobic and hydrophilic surfaces. This analysis is to uncover the hydrophobic effect on the local gas density and local water structure. In the meantime, experiments are carried out to observe visually the effects of a hydrophobic and a hydrophilic surface on gas hydrate formation. The experimental results quantify the effect of surface hydrophobicity on gas hydrate formability. The synergic combination of simulation and experimental data validates HP3. The results from this work are presented in Chapter 7.

HP4: The effect of inorganic ions on gas hydrate formation is governed by ionic sizes and charge density. For example, monovalent ions with small sizes (i.e. fluoride) have high charge density and bind water molecules strongly. These ions are inhibitors to gas hydrate formation. In contrast, monovalent ions with large sizes (i.e. iodide) bind water molecules weakly and are known to induce an increased tetrahedrality of local water on their solvation shells. These ions can be promoters to gas hydrate formation. This hypothesis answers RQ4.

To validate HP4, sodium halides (NaF, NaCl, NaBr and NaI) are chosen as the research subject. Since these salts share the same Na\(^+\) cation, the difference in their effects on gas hydrate formation arises from the halide anions. In other words, the effect of the halide anions on gas hydrate formation can be compared. Since the sizes of halide anions are known (increasing monotonically from F\(^-\) to I\(^-\)), the correlation between ionic sizes and their effect on gas hydrate formation can be deduced. The results of this work are presented in Chapter 8.

HP5: The influence of additives on gas hydrate formation is governed by hydrophobic effect. A hydrophobe in water organises the surrounding water into a clathrate-like structure. The cooperative hydrophobic interactions between the hydrophobe and dissolved gases also create an increased local gas concentration. Thereby, a hydrophobe promotes gas hydrate formation. In contrast, a hydrophilic disrupts the surrounding water structure and competes with the gas for water. Thereby, a hydrophilic inhibits gas hydrate formation. Specially, when the additive is an amphiphile,
the observed effect is a result of the competition between the hydrophobic moiety (a promoter) and hydrophilic moiety (an inhibitor). This hypothesis answers RQ5.

To validate HP5, I used experimental evidence of ion-specific effect of halide ions (as of HP4), the experimental and simulation evidence of the effect of hydrophobic surface and hydrophilic surface (as of HP3), and the evidence of hydrophobic effect from literature. The outcome of this work is presented in Chapter 9.
4.1 Gas hydrate kinetics experiments using a high-pressure reactor

Kinetics experiments were performed to investigate the influence of additives on gas hydrate kinetics. Experiments were carried out using a typical experiment setup for gas hydrate synthesis. The main component was a 450 mL stainless steel reactor (Figure 4.1) which could withstand for a pressure up to 20 MPa. A propeller stirrer (6) was for agitation. The functions of the valves were as follows: valve (3) for evacuating the gas; valve (5) for pressurization of the reactor; and valve (4) for the automatic release in case of over-pressurization. The cooling bath contained glycerine and water with mass ratio of 50:50. The temperature of cooling bath was kept constant at a target value by using a chiller (not shown). The pressure (P) and temperature (T) inside the reactor were simultaneously recorded by a Wika S-11 pressure transducer (Wika, Germany) and a T-type thermocouple (Parr Instruments, USA), respectively. The time-dependent readouts were processed by a National Instruments NI-DAQ 9174 data acquisition device. The digital outputs (T, P) were displayed and saved in the computer in both graphical and numerical forms by using Labview VI software.

Figure 4.1 The scheme of the experiment setup (left) and the real image of the high-pressure reactor and its accessories (right).

Each kinetics experiment was performed in the following procedure. The reactor was initially cleaned three times with DI water (water was purified by using a Milli-Q system) and dried by
compressed air, then partially filled with suitable amount (i.e. 100 mL) of the desired solution. After that, air purging stage was followed to evacuate the initial air from the reactor. Subsequently, the reactor was pressurized to desired pressure (depending on experiments) by compressed gas from a gas cylinder. Once the target pressure was reached, the reactor was quickly disconnected from the cylinder then submerged into the cooling bath. The temperature of cooling liquid was pre-set to a target value (i.e. 0.5 °C). The stirrer was switched on to rotate at a speed of 120 rpm. The instantaneous T and P inside the reactor were recorded and displayed in the computer.

4.2 Induction time, gas uptake and growth rate of gas hydrate formation

In gas hydrate formation, induction time represents the nucleation of gas hydrate [1]. It is theoretically defined as the period from the time when the T-P of a hydrating system reach to hydrate-forming condition till the time when the first hydrate crystal surpasses its critical size. However, it is difficult to determine induction time through this theoretical concept. Alternatively, the induction time is defined as the period between the point when initial cooling completed and the point when the onset of hydrate growth is clearly observed, which is visually shown on Figure 4.2.

![Figure 4.2](image)

**Figure 4.2** The determination of the induction time of gas hydrate formation. Here, the guest used was methane. The experiment was conducted in an isochoric reactor at initial pressure of 7.5 MPa and target temperature set to 0.5°C.

Gas uptake (or gas consumption) is the amount of gas that has been consumed by the hydrate formation. As the reactor was enclosed and no chemical reaction occurred, the total amount of gas inside the reactor remained constant during the experiments and was equal to the amount of gas at the beginning of each experiment \( n_0 \), moles. During an experiment, the gas transferred from the gas phase into the aqueous phase and was consumed by gas hydrate formation. Mass transfer led to a decrease in the amount of gas in the gas phase and was visually indicated by a decrease in the pressure. Gas uptake at time \( t \) was calculated using equation of state of real gas as follows [2]:

\[
P V = n R T
\]
\[
\Delta n(t) = n_0 - n_t = \left( \frac{PV}{ZRT} \right)_{t=0} - \left( \frac{PV}{ZRT} \right)_t
\]  
(4.1)

Where \( n_t \) is the molar amount of gas at time \( t \). \( T \) and \( P \) are the instantaneous absolute temperature and pressure, \( R \) is the universal gas constant, \( V \) is the volume of gas phase which equals to the total volume of reactor deducted by the volume of fluid. \( Z \) is the compressibility factor of gas which is calculated using semi-empirical equations (the Brill-Beggs correlation is used for CH\(_4\) [2] and the Pitzer’s correlations is used for CO\(_2\) [3]).

The growth rate of hydrate, \( r(t) \), was calculated using the gas uptake versus time as follows. The time interval was \( \Delta t = 1 \) minute.

\[
r(t) = \frac{d\Delta n}{dt} \approx \frac{\Delta n(t + \Delta t) - \Delta n(t)}{\Delta t}
\]  
(4.2)

4.3 Visual observation of hydrate formation using a see-through reactor

The system for visual observations of CO\(_2\) hydrate formation is depicted on Figure 4.3. The central part of this system was a 100 mL double-walled stainless steel reactor (Amar Equipment Pvt Ltd, India) which had two transparent quartz windows (2) and could withstand up to 20 MPa. It was cooled by a coolant (glycerol:H\(_2\)O = 50:50) circulating inside the jacket, and could be agitated using a magnetic agitator (8). A set of valves and pipes (5) was also assembled for gas supply, gas release and the safety of operation. The pressure and temperature inside the reactor were recorded by a Wika S-11 pressure transducer (PT) (Wika, Germany) and a T-type thermocouple (TT) (Parr Instruments, USA), respectively. The readouts were then digitalized and displayed on a PC. The optical image-capturing system consisted of a Halogen Lamp Unit (1) (ProSciTech, Australia), an optical lens (3) and a digital camera (4). Inside the reactor, two pre-treated glass surfaces (glass slides) were placed in parallel, as indicated on Figure 4.3b. Of them, one was hydrophobized by treatment with octadecyltrichlorosilane (OTS) and the other was hydrophilized by treatment with potassium hydroxide (KOH). The contact angle (hydrophobicity) of these surfaces is shown on Figure 4.3b.

Each experiment was carried out using the following procedure. First, the reactor was partially filled with 60 mL of DI water (Figure 4.3b) before being cooled to 1 °C and kept constant during the duration of experiment. The initial air inside the reactor was evacuated by blowing CO\(_2\) stream through it. After that, the reactor was quickly pressurized to 6 MPa and maintained at this pressure during the duration of experiments. The CO\(_2\) used was supplied from a G-sized gas
cylinder (98%, Coregas, Australia). Depending on the aim of the experiment, the magnetic agitator was either used or not. When experiments were running, the optical system captured the phenomena happening on the two glass surfaces.

**Figure 4.3** The scheme of experiment setup for studying effects of surface hydrophobicity on gas hydrate formation: (a) the setup of the whole system and (b) the configuration of modified glass surfaces in the hydrate formation cell and their surface hydrophobicity as shown by contact angle.

### 4.4 Sum Frequency Generation vibrational spectroscopy

Sum Frequency Generation (SFG) vibrational spectroscopy was used to probe water structure at gas-solution interfaces (gas was CH₄ or CO₂). SFG is a powerful technique for interfacial probe because it is interface-specific so that any interference of the bulk phase is eliminated [4-6]. Because of this predominant advantage, SFG has been widely used for interfacial probes. Nonetheless, it has not been used in gas hydrate research in previous works. Here SFG was used for the first time to study water structure at gas-solution interfaces in a hydrate-related research.

SFG 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 gas-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. 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 α_vis = 60° and that of the IR set to α_IR = 54°. The signal was fine-tuned at 3200 cm⁻¹ for 3000-3600 cm⁻¹ region.
Figure 4.4 shows the scheme of sampling system for probing methane-solution interface, for example. Methane was charged into the sampling cell prior to the measurement. The sampling cell consists of a cap (1) and a base (2). The cap has two transparent CaF$_2$ crystal windows (5) which allow the laser beams to travel through. The cell was also assembled to an external mechanical rig (not shown) for adjusting the configuration. For the interpretation of the spectra, the experimentally measured signals were fitted with theoretical modulus model of SFG spectroscopy.

![Figure 4.4 Sampling system for recording SFG signal for methane-solution interface, consisting of: cell cap (1), cell base (2), sample base (3), solution (4), transparent CaF$_2$ crystal windows (5), O-ring (5), inlet (7) and outlet (8) of methane stream.](image)

4.5 Attenuated total reflectance Fourier-transform infrared spectroscopy

Attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectroscopy was employed to probe the structure of water in the bulk phase. ATR-FTIR was 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 surfactant 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).

4.6 Molecular dynamics simulation

Molecular dynamics (MD) simulations were employed to analyze surface adsorption of surfactants, the alignment of interfacial water, the tetrahedral order of water and the local concentration of gases. The results from MD were used to support or validate the interpretation of SFG and ATR-FTIR data.
In my simulations, the molecular models were created using AmberTools14, and molecular dynamics simulations were performed in Amber9 software [7, 8]. TIP4P-ew was used for water model [9]. Hydrocarbon molecules were modelled by using the all-atoms carbon model with hydrogen atoms being explicitly described [10]. The molecular parameters (bonds, angles, and torsions) were retrieved from General Amber Force Field (GAFF) and literature [11, 12]. Simulation systems were created by inserting molecules into simulation boxes using Packmol package [13]. Simulations were performed using computational resources at Pacific Northwest National Laboratory, USA. The simulations were performed with different systems including gas-solution interfaces and solid-water interfaces. The details of these systems are described below.

4.6.1 Simulation of gas-solution interfaces

This simulation was used to study the effects of surface adsorptions of surfactants on interfacial water structure. The results were then applied to support the interpretations of spectral and kinetics data. Figure 4.5 presents a typical example of simulation system of gas-solution interface (the gas was either CO₂ or CH₄). The simulation box was an orthogonal box with x, y, z dimensions being 50, 50, 100Å, respectively. It was divided into three spatial zones with respect to z-axis. H₂O and the additive molecules (when applicable) were inserted randomly into 15 Å ≤ z ≤ 85 Å zone and formed an aqueous solution while the gas occupied the rest of the box. This configuration produced two gas-solution interfaces at z_{low} = 15 Å and z_{high} = 85 Å, respectively. The number of additive molecules in simulation boxes was chosen to produce a desired concentration (depending on each simulation). Simulations were run with NPT ensemble with T and P were set to desired values (e.g., 274 K and 7.5 MPa). The temperature coupling was controlled using the Langevin dynamics scheme and the pressure scaling was controlled using the Berendsen barostat. The cut-off radius of Lennard-Jones interactions was 11 Å. The Ewald summation technique was used to handle long-range electrostatic interactions and the SHAKE algorithm to fix the internal molecular geometry [14].

The outputs from simulations were used to compute the surface adsorption of surfactants (SDS and TBAB) and the orientation of interfacial water molecules underneath the solution’s surface. The calculation of surface adsorptions of surfactants is presented in Section 11.1.3 (Appendix). The orientation of water molecules with respect to surface normal (z-axis) was calculated by using Eq. (4.3). In this equation, the orientation parameter \( \langle \cos \varphi \rangle \) indicates the average of water dipoles with respect to z-axis. The physical meaning of \( \langle \cos \varphi \rangle \) is that it indicates the change in the average orientation of local water molecules along surface normal from gas phase to water phase. To calculate \( \langle \cos \varphi \rangle \), the simulation box was divided into different slabs in parallel
with the xy plane, and each slab had a thickness of 1 Å. In each slab, \( \langle \cos \varphi \rangle \) was calculated using Eq. (4.3) where \( \varphi \) was the angle between the z-axis and dipole vector of the water molecule; \( N_{\text{water}} \) was the number of water molecules in the current slab and \( \Delta z \) was the distance from the current slab to the Gibbs dividing surface (see Section 11.1.3 for the definition of Gibbs dividing surface and Figure 4.6 for the definition of the angle \( \varphi \)).

**Figure 4.5** Example of a simulation box for study the gas-solution interface. In this example, the additive is tetra-butyl ammonium bromide which consists of tetra-butyl ammonium (TBA\(^+\)) cation and Br\(^-\) anion. The system has two gas-solution interfaces at \( z_{\text{low}} = 15 \) Å and \( z_{\text{high}} = 85 \) Å. The gas molecules are hidden for clarity.

\[
\langle \cos \varphi \rangle_{\Delta z} = \left\langle \frac{\sum \cos \varphi}{N_{\text{water}}} \right\rangle_{\Delta z}
\]  

**Figure 4.6** The definition of \( \varphi \) in this work.

**4.6.2 Simulation of solid-water interfaces**

This simulation was used to compute the local gas density and local water structure at solid-water interfaces. The simulation results were then applied to elucidate the effects of hydrophobic solid particles on gas hydrate formation. The simulation comprises several steps as follows.
**Building hydrophobic solid surface:** The hydrophobic solid particles used in gas hydrate experiments are usually silica-based substrates [15, 16]. The surfaces of these particles are hydrophobized by alkylation to produce an alkyl-grafted layer coating the surfaces [17], as schematically depicted in Figure 4.7a. When hydrophobic particles are used as gas hydrate promoters, the grafted alkyl layer determines the hydrophobicity of the surface and therefore directly influences the formation of gas hydrates.

The grafted alkyl layer was simulated in my simulation. To create alkylated solid in simulation, I used Packmol software [13] to place octane molecules into a fashion so that every molecule was in parallel with each other. In order to generate solid state, frozen technique was used [7]. In a frozen state, translational and rotational motions of every octane molecule were completely removed, yet every atom in each molecule was allowed to vibrate about its initial Cartesian coordinates under a harmonic potential. The resulting surface was called the OTA surface.

**Building hydrophilic solid surface:** To create a hydrophilic solid surface, I replaced the terminal methyl CH₃ groups on the OTA surface by carboxyl COOH groups. The resulting surface was called the COO surface.

**Building solid-water interface:** To create hydrophobic solid-water interface, I placed 5400 water molecules and a desired number (e.g., 30, 120 and 210) of CH₄ (or CO₂) molecules onto the OTA surface. The resulting simulation box had its initial x-, y-, z-dimensions of 42, 42, 120 Å, respectively. An example of the created system is shown on Figure 4.7b. Similarly, hydrophilic solid-water interface was built using the same manner except the solid being COO surface instead of OTA.

![Figure 4.7](image)

**Figure 4.7** A scheme of a real alkyl-grafted solid surface (a) and an example of simulated hydrophobic solid-water interface built for my simulation (b). The fixed hydrocarbon layer in simulation box (image b) is to mimic the alkyl-grafted layer in the real system (image a). For the image (b), it is noted that this is the initial configuration, and it only shows the bottom part of simulation box (as the top part is truncated for better clarity of the interface).
**Running solid-water interface simulation:** For each simulation, after running energy minimization, molecular dynamics was performed for 30 (ns) with a time step of 2 (fs). Simulations were run with NPT ensemble with temperature coupling controlled using the Langevin dynamics scheme and pressure scaling controlled using the Berendsen barostat. The cutoff radius of Lennard-Jones interactions was 11 Å. The temperature and pressure were set to 274 K and 60 at (6 MPa), respectively. Harmonic constant for frozen atom vibration was 20 kcal/mol. The SHAKE algorithm was used to fix the internal molecular geometry. For analysis of molecular trajectories, the last 10 (ns) of total 30 (ns) was taken into calculation (because this was the period in which simulation was running in equilibrium status).

4.6.3 **Simulation of contact angle**

This simulation was supplemental to the solid-water simulation. It was used to evaluate the hydrophobicity of the simulated surfaces from the above section. Contact angle simulation was performed using a method similar to that being described in details elsewhere [18, 19]. In a brief description, a droplet (spherical cluster containing 1100 water molecules) was initially placed on a simulated surface (either the OTA or COO surface). Then, the simulation was started with $10^4$ steps of energy minimization, followed by $10^6$ steps (or 2 ns) of molecular dynamics under NVT ensemble.

![Figure 4.8](image)

**Figure 4.8** The method for determining the contact angle between a simulated solid surface and a water droplet. Simulation snapshot (left) show an instantaneous shape of the water droplet on simulated surface. Some vaporised water molecules are seen from this snapshot. The density profile of the water droplet (right) shows the mean boundary of the droplet. The contact angle is estimated by extrapolating the fitting curve to the solid surface, as indicated.
The left panel of Figure 4.8 shows a snapshot of the water droplet (drawn in dark blue). From this snapshot, the contact angle can be evaluated. However, as the water cluster was very dynamic due to thermal motions, the contact angle fluctuated slightly with time. To calculate the accurate contact angle, the droplet was divided into different layers in parallel with the solid surface, and each layer had a thickness of 3 Å. In each layer, I calculated the radial density profile. From the obtained radial density profile, I determined the mean radius \( r \) of the each layer. Finally, I plotted \((z, r)\) graph as shown on right panel of Figure 4.8. The fitting curve represents the mean boundary of the water droplet. The contact angle was accurately calculated by extrapolating the fitting curve to the solid surface \((z = 0)\), as indicated.

References


Chapter 5

Unexpected Inhibition of CO$_2$ Hydrate Formation in Dilute TBAB Solution and the Critical Role of Interfacial Water Structure\textsuperscript{1}

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 I report unexpected experimental results which show that TBAB inhibits CO$_2$ gas hydrate formation when used at minuscule concentration. I 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. I explain this finding using the concept of activation energy of gas hydrate formation. These results provide a step toward to mastering the control of gas hydrate formation.

\textsuperscript{1} Published in Fuel 185 (2017) 517-523
5.1 Background context

Tetra-n-butylammonium bromide (TBAB) is one of the most attractive hydrate promoters owing to its high effectiveness. The body of previous research on this additive was enormous yet it focused primarily on high-concentration regime. For this range of concentration, TBAB has been consistently reported as an effective promoter [1-3]. Moreover, previous works targeted the macroscopic measurements of TBAB effects on kinetics and thermodynamics of gas hydrate formation while the science underlying the experimental observations remains poorly understood. The conventional way to explain the promoting behaviour 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 further investigations using both experimental and computational techniques. In this work, I examined the influence of TBAB of a wide range of concentration, from several mM to several M, on the formation of CO₂ gas hydrates. I observed an unexpected inhibition effect of TBAB at an ultralow concentration (around 0.125% by wt. or 3.8 mM), contrasting to the well-known promotion behaviour of concentrated TBAB solutions. This inhibition effect of TBAB is extraordinary and, therefore, is of fundamental importance. Specifically, I 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, I also utilized molecular dynamics (MD) simulation to qualify my spectral interpretation. The synergic combination of spectral and computational results signifies the interplay of water orderliness at the gas-solution interface 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.

5.2 Unexpected inhibition of CO₂ hydrate formation in dilute TBAB solutions

Figure 5.1 shows typical changes in the instantaneous pressure (P) and temperature (T) versus time for CO₂ 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 CO₂ in water. At the same time, the temperature increased swiftly from initial value of around 1.5ºC to about 3ºC as a result of the system being warmed up by sensible heat of the feed gas as well as latent heat of CO₂ dissolution. Within the next 10 minutes, the pressure remained constant while the temperature decreased to around the initial value, indicating that the dissolution of CO₂ in water.
was completed. Then, the pressure started to drop substantially for the second time while the temperature increased suddenly. The second decrease in pressure was caused by the uptake of gas by gas hydrate formation while the second 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 CO\textsubscript{2} gas hydrate was approaching the completion.

![Figure 5.1](image.png)

**Figure 5.1** Typical changes in the instantaneous pressure \((P)\) and temperature \((T)\) versus time for CO\textsubscript{2} hydrate formation. The concentration used was 3\% TBAB (by weight). The second drop in \(P\) and the rise in \(T\) provide strong evidence of the exothermal formation of CO\textsubscript{2} hydrate.

Figure 5.2 shows the experimental results for CO\textsubscript{2} uptake versus TBAB concentration and time. The CO\textsubscript{2} uptake increased with time as expected. The dependence of the gas uptake on TBAB concentration is interesting and surprising. With the increase in TBAB concentration, the gas uptake decreased first, going through a minimum (achieved at \(C_{TBAB} = 0.125\) weight \%), and then increased to a maximum level in high concentration. The increased gas uptake at high TBAB concentration is well reported in the literature and is assigned to the promotion of gas hydrate formation by TBAB [1-3]. The decreased gas uptake at \(C_{TBAB} = 0.125\)\% (by wt.) is extraordinary and interesting. For example, the gas uptake after 300 minutes by 0.125\% TBAB solution was 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 increase gas consumption by 14\%, from 0.044 (mol/mol water) to 0.050 (mol/mol water). Evidently, the dilute solution of 0.125\% TBAB displayed an inhibition effect on the CO\textsubscript{2} uptake which has not been reported previously and is unexpected. This is an interesting finding of this work.
Figure 5.2 Experimental results for CO$_2$ uptake versus TBAB concentration and time: The dual effect of TBAB on the formation of CO$_2$ hydrate. 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 CO$_2$ 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 was calculated using the measured gas uptake shown in Figure 5.2. The results for the growth rate are shown in Figure 5.3. Similar to the gas uptake, the growth rate of CO$_2$ hydrate also underwent the same dual pattern of TBAB concentration dependence (Figure 5.3). 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 CO$_2$ 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 5.3 since the other concentrations show the similar trend.

Although the promoting effect of TBAB on gas hydrate formation is widely reported in the literature [1-3], 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 5.3 The rate of CO₂ 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 that the growth rate in solutions of high TBAB concentrations.

5.3 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 [4-7] while in ATR-FTIR technique, the incident beams can penetrate into bulk phase (through a depth of 1 µm) to signify the structural property of the bulk [8]. Hence, SFG and ATR-FTIR provide an excellent combined tool to gain a full picture of changes in water structure [7] and correlate them with the experimental results. In particular, I focused on the changes in water structure of low and high TBAB concentration solutions.

5.3.1 Dual effect of TBAB on water structure at the gas-solution interface

The left panel of Figure 5.4 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 OHs (water hydroxyl groups) 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 5.4 shows the intensity of this peak versus TBAB concentration. The substantial increase in the peak intensity at low TBAB concentrations manifests the increasing alignment of water molecules at the surface of dilute TBAB solutions [6, 9]. Likewise, the decrease in the peak intensity at high TBAB concentration shows that water
became less aligned at the surface of concentrated solution compared to that of dilute TBAB solutions. Evidently, this change in interfacial water structure correlates well with the change in the gas uptake presented in Section 5.2.

Figure 5.4 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 (the peak height) at low TBAB concentrations manifests the increasing alignment of water at the surface of dilute TBAB solutions. The decrease in the SFG amplitude signal at high TBAB concentration shows that water became less aligned at the surface of concentrated solution compared to that of dilute TBAB solutions.

5.3.2 Effect of TBAB on water structure in the bulk

Figure 5.5 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 [6, 10, 11]. Their intensities were found to be proportional to TBAB concentration in the solutions (see Section 11.1.2, Appendix). This feature of alkyl regime confirms the reliability and bulk-specificity of the measured ATR-FTIR spectra. The two broad peaks at 3200 cm\(^{-1}\) and 3400 cm\(^{-1}\) present the characteristic stretches of hydrogen-bonded OHs of bulk water. They are significant to the understanding the effect of TBAB on gas hydrate formation.

As can be seen from Figure 5.5, the magnitudes of these two peaks are significantly influenced by TBAB concentration. The peak of the weakly hydrogen-bonded OHs 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.

**Figure 5.5** 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 OHs in the solutions and weakened the peak at 3200 cm\(^{-1}\) for strongly hydrogen-bonded OHs.

On the contrary to the weakly hydrogen-bonded OHs at 3400 cm\(^{-1}\), the off-set absorbance of the strongly hydrogen-bonded OHs at 3200 cm\(^{-1}\) is negative as shown in Figure 5.5. It is an evidence of the weakening of the ATR-FTIR signal of the strongly hydrogen-bonded OHs 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.

These experimental ATR-FTIR results (showing the increase in the 3400 cm\(^{-1}\) peak for weakly hydrogen-bonded OHs and the decrease in the 3200 cm\(^{-1}\) peak for strongly hydrogen-bonded OHs) provide a solid evidence of the significant effect of TBAB on weakening the
hydrogen bonded network of the bulk water. These ATR-FTIR results together with the SFG results help explain the experimental observations presented in Section 5.2 as to be discussed shortly in Section 5.4

5.3.3 Results of molecular dynamic (MD) simulation

Figure 5.6 Simulation box for study surface adsorption of TBA\(^+\) cations at gas-solution interfaces. The x, y, z dimensions of the box were 50Å, 50Å, 100Å, respectively. Two gas-solution interfaces located at \(z_{\text{low}} = 15\text{Å}\) and \(z_{\text{high}} = 85\text{Å}\). The TBA\(^+\) and Br\(^-\) ions were initially inserted randomly into the aqueous zone of the simulation box. The gas phase is hidden for a better clarity.

In the solution, TBAB dissociates into tetra butyl ammonium cation (TBA\(^+\)) and Br\(^-\) anion (Figure 5.6). The TBAB molecules (consisting of TBA\(^+\) and Br\(^-\)) were inserted randomly into the aqueous zone (15Å ≤ \(z\) ≤ 85Å) of simulation boxes at the beginning of the simulation, as shown on Figure 5.6 (see Section 4.6.1 for simulation method). The total concentrations (\(C_t\)) of TBAB in simulation boxes were 0.095 M (low), 0.142 M (intermediate) and 0.285 M (high), which were denoted as Systems A, B and C, respectively. Based on the simulation outputs, I calculated the local concentrations of TBA\(^+\) at the interfaces (\(C_i\), also known as surface excess) and in the bulk (\(C_b\)) of the aqueous phase for each total concentration (\(C_t\)), see Section 11.1.3 (Appendix) for details of calculation method.

Figure 5.7 shows the calculated concentrations of TBA\(^+\) at the interfaces (\(C_i\)) and in the bulk (\(C_b\)) of simulation boxes for the three total concentration (\(C_t\)) of TBAB. 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 \(C_i = 0.33\ \mu\text{mol/m}^2\) and negligible concentration of TBAB remaining in the bulk solution, \(C_b = 0\text{ M}\). However, when \(C_t\) increases to 0.142 M (System B), \(C_i\) increases to 0.40 \(\mu\text{mol/m}^2\) 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), $C_t$ continues to increase to 0.73 μmol/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, the computed surface excess is comparable with that of common surfactants like tetradecyl trimethyl ammonium bromide (0.8 – 1.6 μmol/m$^2$) [12] or sodium dodecyl sulfate (0.1 - 5 μmol/m$^2$) [13].

**Figure 5.7** The results of MD 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 aqueous phase 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.

Evidently, TBAB surfactant is strongly surface-active. The ions of TBAB and water were initially packed randomly in the aqueous zone $15\text{ Å} \leq z \leq 85\text{ Å}$. With increasing the simulation running time, TBA$^+$ cations underwent thermal motion and moved to the interfaces where they were retained (adsorbed) to minimize their free energy, resulting in an enrichment of TBA$^+$ at the interfaces. Experimentally, the presence of TBA$^+$ cations at the solution surface was evidenced through the occurrence of alkyl vibration modes on SFG spectra (see Section 11.1.1, Appendix).

The MD simulation results quantitatively show a significant effect of total TBAB concentration on the TBA$^+$ concentration at the solution surface and in the bulk phase. Importantly,
my 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 5.7 (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 the aqueous phase of simulation box). Secondly, when interfacial concentration of TBA$^+$ reaches 0.4 $\mu$mol/m$^2$, the concentration of bulk-residing TBA$^+$ 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 gas-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 5.7.

These simulation cases correspond to the experiments of gas hydrates, SFG and ART-FTIR spectroscopy at low 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 change in the interfacial water structure is rapid (as revealed by the SFG spectra, Figure 5.4) but the change in the bulk water is insignificant (as confirmed by the ATR-FTIR spectra, Figure 5.5). However, when the added TBAB concentration is high, the concentration of TBA$^+$ cations residing in the bulk solution is increased as per the simulation results. It leads to the weakening of hydrogen bond network in the bulk as evidenced by the ATR-FTIR results in Figure 5.5.

5.4 General discussion

The obtained 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. Strongly hydrogen-bonded OHs vibrate at a lower frequency while weakly hydrogen-bonded OHs vibrate at a higher frequency [14]. Indeed, it is known that the spectral band at 3200 cm$^{-1}$ arises from strongly hydrogen-bonded water and explicitly manifests the aligned state of water while the band at 3400 cm$^{-1}$ arises from weakly hydrogen-bonded water and, therefore, it manifests the water with a lesser degree of hydrogen bond [15-17]. Specifically, the spectral increase at 3200 cm$^{-1}$ in SFG spectra (Figure 5.4) is assigned to an increased water alignment at the surface of dilute TBAB solution [6, 9]. Likewise, spectral decrease at 3200 cm$^{-1}$ and increase at 3400 cm$^{-1}$ in ATR-FITR spectra (Figure 5.5) indicate a weakened water structure in
the bulk TBAB solution of high concentration [14]. This spectral information about water structure is helpful in understanding the effect of TBAB on inhibiting and promoting gas hydrate formation as discussed below.

My results show the significant changes in gas hydrate kinetics and in 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 a strong water alignment at the interface and a significant reduction in hydrate kinetics are evident (both at 0.125% TBAB). Therefore, the water alignment at the gas-solution interface is responsible for gas hydrate inhibition. This aspect of the unexpected gas hydrate inhibition and its link to water alignment at the gas-solution interface has not been reported previously. This observation also implies an important role of interfacial water in governing gas hydrate formation. This finding can be explained based on the fundamentals of gas hydrate formation. Accordingly, gas hydrate formation is a successive transformation of water structure from a liquid state into the clathrate-like solid state [18, 19]. In this process, water molecules have to rearrange themselves to accommodate the gas molecules. As the nucleation takes place at the gas-water interfaces [20-22], the local water molecules needing to rearrange themselves are those at the interfaces. Thus, initially strongly hydrogen-bonded (aligned) water at the interface between gas and dilute TBAB solution is unfavorable for the rearrangement. Otherwise, it would require a higher driving force to surpass the interaction between water dipoles and external electrostatic field (which 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 in the bulk solution. As per simulation results, most of TBA+ cations reside in the bulk phase 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 (Figure 5.5). A similar weakening of water structure around some other hydrophobic solutes is also discussed in the literature [23, 24]. 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 CO2 hydrate. Therefore, TBAB used with a high concentration becomes a promoter of gas hydrate formation.

5.5 Conclusion

In this chapter, I have successfully conducted the combined kinetic experiments, spectroscopic measurements, and computer simulation to study the effect of TBAB on CO2 hydrate
formation and its underlying mechanisms. The kinetic data show an unexpected inhibition of CO$_2$ hydrate formation observed at ultralow concentration of TBAB (around 0.125% by wt.) besides a commonly known hydrate promotion reported for high concentration of TBAB. The insightful observations from interface-specific SFG spectra and bulk-specific ATR-FTIR spectra with the support from MD simulation have revealed the critical role of water alignment underneath surface adsorption of TBA$^+$ cations in inhibiting CO$_2$ hydrate formation in dilute TBAB solution. The obtained results also suggest that the perturbation of water induced by bulk-residing TBA$^+$ cations promotes CO$_2$ hydrate formation in high-concentration solution of TBAB. I explain my 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 additives in controlling gas hydrate formation, an emerging method for separation, storage and transportation of gases.

References


Chapter 6

The Inhibition of Methane Hydrate Formation by Water Alignment underneath Surface Adsorption of Surfactants

Abstract

Sodium dodecyl sulfate (SDS) has been widely shown to strongly promote the formation of methane hydrate. Here I show that SDS displays an extraordinary inhibition effect on methane hydrate formation when the surfactant is used in sub-millimolar concentration (around 0.3 mM). I have also employed Sum Frequency Generation (SFG) vibrational spectroscopy and molecular dynamics (MD) simulation to elucidate the molecular mechanism of this inhibition. The SFG and MD results revealed a strong alignment of water molecules underneath surface adsorption of SDS in its sub-millimolar solution. Interestingly, both the alignment of water and the inhibition effect (in 0.3 mM SDS solution) disappeared when an oppositely-charged surfactant (tetra-n-butylammonium bromide, TBAB) was suitably added to produce a mixed solution of 0.3 mM SDS and 3.6 mM TBAB. Combining structural and kinetic results, I pointed out that the alignment of water underneath surface adsorption of dodecyl sulfate (DS') anions gave rise to the unexpected inhibition of methane hydration formation in sub-millimolar solution of SDS. The adoption of TBAB mitigated the SDS-induced electrostatic field at the solution’s surface and, therefore, weakened the alignment of interfacial water which, in turn, erased the inhibition effect. I discussed this finding using the concept of activation energy of the interfacial formation of gas hydrate. The findings of this work reveal the interplay of interfacial water in governing gas hydrate formation which sheds light on a universal molecular-scale understanding of the influence of surfactants on gas hydrate formation.

2 Published in Fuel 197 (2017) 488-496
6.1 Background context

Sodium dodecyl sulfate (SDS) is the best known hydrate promoter [1-4]. It has been widely used as a model surfactant in gas hydrate research. The use of SDS at a concentration of several CMC (critical micellar concentration) can increase the rate of gas hydrate formation by 700 times [5]. Even though, the mechanism behind the promotion effect is controversial. The explanation for the promotion effect has mostly relied on the assumption that surfactant micelles in the solution act as minute gas reservoirs and provide nucleation sites for gas hydrate formation [5]. In another hypothesis, the promotion effect of surfactants is attributed to the decreased interfacial tension of hydrate-solution interface due to the surfactant adsorption [6]. However, it was also found that SDS could act as an inhibitor of gas hydrate formation in certain conditions [7]. In fact, the inhibition effect of SDS is extraordinary and cannot be elucidated by using the available literature. The current context reflects a major knowledge gap in understanding the mechanism of surfactant effects on gas hydrate formation. Indeed, one critical shortcoming of the existing literature is the negligence of the role of the interfacial water structure in gas hydrate formation. In Chapter 5, I demonstrated that tetra-butyl ammonium bromide (TBAB) at ultralow concentration acts as a hydrate inhibitor. Here, I conducted a systematic investigation into the effect of SDS of a wide concentration range (from sub-millimolar to millimolar) on methane hydrate formation. Interface-specific Sum frequency generation (SFG) vibrational spectroscopy and molecular dynamics (MD) simulation were used to analyze the interfacial water at methane-solution interfaces in relation to gas hydrate kinetics. The obtained results together with the results presented in Chapter 5 provide concrete evidence of the critical role of the interfacial water in governing gas hydrate formation.

6.2 Effect of SDS on methane hydrate formation kinetics

**T-P graphs:** Figure 6.1 shows a typical change in the temperature (T) and pressure (P) versus time recorded from the hydrate reactor. Typically, the duration of each experiment can be divided into four distinct periods. The first stage encompassed the first several minutes of the experiment course in which both P and T dropped sharply. The drops in pressure and temperature in this stage were mainly induced by the gas contraction and gas dissolution due to cooling (when the reactor was being submerged into the cooling bath). After a few minutes, the temperature remained constant at around 0.5 ºC, indicating that the cooling period had finished and was followed by an induction period. In the induction stage, the temperature remained constant, while the pressure continued to decrease steadily, indicating the ongoing dissolution of methane into water. This awaiting period was for the creation of a supersaturated gas in water which was needed for gas hydrate nucleation. Also during this time, water molecules rearranged to accommodate the gas and
transformed into a pre-clathrate-like conformation which could be considered as the evolution of gas hydrate nucleation. The duration of this period (called the induction time) varied greatly with the change in experiment condition. After that, growth stage was following. Apparently, the initiation of growth stage was signified by a catastrophic drop in the pressure along with a sharp rise in the temperature, both due to the exothermic formation gas hydrate inside the cell. Eventually, both P and T approached constant levels, indicating that the system was reaching equilibrium stage and hydrate formation finished.

Figure 6.1 Typical P-T profile showing the change in pressure and temperature versus time during methane hydrate formation. The experiment was performed in an isochoric system. The initial pressure was 75 atm (7.5 MPa) and the target temperature was set to 0.5 °C

**Induction time**: In gas hydrate formation, induction time represents the nucleation of gas hydrate [8]. It is theoretically defined as the period from the time when the T-P of a hydrating system reach to hydrate-forming condition till the time when the first hydrate crystal surpasses its critical size. At a molecular scale, it is the time needed for gas to dissolve into water to produce a supersaturated solution and for water structure to rearrange itself to accommodate the gas and form initial hydrate crystals. However, it is difficult to determine induction time through this theoretical concept. Alternatively, the induction time can be practically described by the period between the point when initial cooling completed and the point when the onset of hydrate growth is clearly observed, which is visually illustrated in Figure 6.1.

Figure 6.2 presents the induction time of methane hydrate formation versus the concentration of SDS. It is noted that, at some important concentrations, the experiments were repeated three to five times to determine the standard deviation and the reproducibility of the data. The obtained data on Figure 6.2 show that the average induction time of methane hydrate formation in neat water was 7.35 (hour). When the concentration of SDS was increased, the induction time increased first and
then leveled off at 20.44 (hour) at 0.3 mM. Beyond this concentration, the induction time decreased continually with the increase of the concentration of SDS. In particular, the concentration of 5 mM SDS gave an induction time of 0.23 hour, giving a 32-fold reduction compared to the case of pure water.

![Figure 6.2](image)

**Figure 6.2** Induction time of methane hydrate formation in SDS solution of different concentrations. The data show an extraordinary inhibition observed at the concentration around 0.3 mM, along with a well-known promotion observed in concentrated SDS solution.

**Gas uptake:** In complement with the data about induction time, Figure 6.3 presents the normalised methane uptake by the hydrate as a function of time and SDS concentration. On the figure, a blue bay between 0.1 mM and 0.5 mM indicates a low gas uptake domain, while the red displays a region with high gas uptake. For example, at the SDS concentration of 0.3 mM, the color profile remains blue after 20 hours, indicating that gas uptake was still insignificant at that time. In contrast, at 5 mM, the color profile becomes red after a very short time, showing that high methane uptake was achieved shortly after the experiment started. Nonetheless, it is seen that the accumulative gas uptake after 24 hours is almost similar for every concentration of SDS (and being around 0.11 mole CH₄ per mole water). This observation indicates that although the induction time was strongly affected, the final methane uptake was not affected significantly. This is because, as per my observation, the water in the reactor was fully consumed after 24 hours and, hence, the methane uptake was terminated due to the shortage of water.
Figure 6.3 Time-dependent methane uptake by hydrate formation in SDS solution of different concentrations. A blue bay shows a domain of low methane uptake in the concentrations between 0.05 mM and 0.5 mM. In high concentration region, the colour profile becomes red after few minutes, indicating the promoted hydrate formation with high methane uptake.

From the results about induction time and methane uptake, it is being shown that the dilute solution of SDS (especially at 0.3 mM) induces a strong inhibition of the formation of methane hydrate. In high-concentration regime, SDS becomes an effective promoter. Although the promotion of gas hydrate formation by SDS is well known in the literature, the strong inhibition found in sub-millimolar concentration is extraordinary and fundamentally important. It implies that the affecting mechanism of SDS on gas hydrate formation needs to be carefully reconsidered. In the following sections, I used spectroscopic and simulation means to elucidate the underlying mechanism of this peculiar observation.

6.3 Effect of SDS on interfacial water structure (SFG spectra)

Sum Frequency Generation vibrational spectroscopy (SFG) was employed to study water structure at methane-water interfaces in the search for the origin of the inhibition observed in dilute SDS solution. SFG spectra are interface-specific and have been widely used for interface research, even though it was not used in gas hydrate-related studies.

Figure 6.4a shows a typical SFG spectrum of a methane-SDS solution interface, recorded in the 3000 - 3600 cm\(^{-1}\) region. This region is of particular interest in this work as it is characteristic to the hydrogen-bonded water network [9, 10]. On the figure, the experimental (measured) SFG data is shown in red circles, and the fitting of experimental data with modeled SFG is shown in solid black line. The green and blue curves, respectively, show the intensities of the two component peaks which constitute the spectral feature of this region. The center and the intensity of each peak were determined via fitting experimental data with SFG modules (see Section 11.2.1, Appendix)
The data from SFG spectra. (a): a typical of experimental SFG spectra and its fitting components, and (b): the intensity of each component peak and the ratio between them as a function of SDS concentration. From graph (b), strong hydrogen bonds of water at the surface of 0.3 mM SDS solution is evidenced.

In Figure 6.4a, two broad peaks centered at 3220 and 3445 cm\(^{-1}\) are clearly identified. Although the configurational assignment of these peaks remains controversial [10-15], it is factual that strongly-hydrogen-bonded OHs and weakly-hydrogen-bonded OHs, respectively, vibrate at lower and higher frequencies [10, 16]. In accord with this general principle, the first peak centered at 3220 cm\(^{-1}\) is attributed to strongly hydrogen bonded OHs and, thus, manifests an ordered (oriented) configuration of water network [17, 18]. Likewise, the second peak centered at 3445 cm\(^{-1}\) is assigned to weakly hydrogen bonded OHs and, therefore, is an indicator of a disordered configuration of water [18-20]. It should be, however, noted that in this context the ordered configuration does not mean the water network is more tetrahedrally coordinated. Instead, it just means an enhancement in the intermolecular interaction between water molecules, which point will be clarified through this chapter. Also in Figure 6.4a, the symbols I(s) and I(w) denote the intensity of the two peaks. As per the above assignments, the I(s)/I(w) ratio can be used as a measure of the ordering and hydrogen bond strength of the interfacial water [21]. For this reason, both the I(s)/I(w) ratio and its individual components are shown in Figure 6.4b as a function of the concentration of SDS. From Figure 6.4b, two opposite patterns on the evolution of I(s)/I(w) are observed. In sub-millimolar concentration, the ratio increases rapidly with the increase in SDS concentration and this increasing trend progresses until the concentration reaches 0.3 mM. From this point, the I(s)/I(w) turns to decrease continually with the concentration further increasing. Structurally, these spectral results reveal different effects of SDS on water structure at the interface. On one hand, the presence of SDS of sub-millimolar concentration results in an enhancement in water ordering and hydrogen bonds at the methane-solution interface. On the other hand, high concentrations of SDS lead to a depression of interfacial water followed by a weakening of hydrogen bonds.
6.4 Simulation results

The method of simulation was described in details in Section 4.6.1. Figure 6.5 shows an example of the initial configuration of a methane-solution interface used in my simulation. Dodecyl sulfate (DS⁻) anions and Na⁺ counter ions were inserted randomly into the aqueous phase and CH₄ molecules were inserted in the gas phase of the simulation box. Four simulation systems with the total concentration of SDS of 0 (pure water), 0.095 M (System A), 0.190 M (System B) and 0.285 M (System C) were investigated. These concentrations were defined as the molar amount of SDS divided by the volume of the aqueous phase in simulation box (in liter). When the simulation was running, all molecular species underwent thermal motions. The DS⁻ anions moved to the interface and adsorbed on there. Based on the output of simulation, I calculated the density profiles of water and DS⁻ ions with respect to the z-axis. The orientation of local water molecules was also computed using Eq. (4.3) in Section 4.6.1.

![Diagram of simulation box configuration](image)

**Figure 6.5** An example of the initial configuration of simulation box for a methane-solution interface. At the beginning of the simulation, SDS surfactant (DS⁻ and Na⁺) were inserted randomly in the aqueous phase with water. Methane molecules were in the gas phase.

Figure 6.6a shows an example of simulation results for the interface between methane and SDS solution of 0.095 M (System A). On the graph, the blue circles show the computed density of water and the blue line shows the fitting of the data using tanh function

\[ \rho_{H,O} = a \times \left\{ 1 + \tanh \left[ b \times (\Delta z - c) \right] \right\}, \]

in which \( a = 27.50 \), \( b = 0.50 \) and \( c = 0 \). The origin of the horizontal axis (\( \Delta z = 0 \)) indicates the position of Gibbs dividing surface (GDS). The left side of the GDS (\( \Delta z < 0 \)) indicates the gas phase, and the right side (\( \Delta z > 0 \)) indicates the liquid phase. The red squares show the density profile of DS⁻ anions. From this density profile, a strong surface
adsorption of DS\(^{-}\) is shown by the enrichment of this anion in the interfacial region. Also on Figure 6.6a, the green squares indicate the orientational parameter, \(\langle \cos \varphi \rangle\), calculated from Eq. (4.3). By definition, this parameter provides a measure of water alignment at methane-solution interface and, therefore, is of central interest in this work. Evidently, the value of \(\langle \cos \varphi \rangle\) varies greatly along the surface normal. It is significantly negative (namely -0.4) in the gas phase region near Gibbs dividing surface (GDS) which feature indicates that vaporised water molecules tend to point their hydrogen atoms towards gas phase. Similarly, the negative \(\langle \cos \varphi \rangle\) (namely -0.1) in the sub-surface region indicates that the local water molecules are aligned into a configuration so that the molecular dipoles tend to point towards the bulk liquid (or hydrogen atoms pointing towards the interface). At a distance far from the GDS, \(\langle \cos \varphi \rangle\) approaches to zero which implies that the bulk condition has been reached. For convenience in later discussion, I define the interfacial depth as the region spreading from GDS to somewhere in the liquid phase at which \(\langle \cos \varphi \rangle\) neutralized.

**Figure 6.6** Properties of methane-solution interface obtained from simulation. (a) An example of interfacial properties calculated from simulation and (b) the dependence of orientational parameter upon the total concentration of SDS in simulation box. The total concentration is defined as the molar amount of SDS divided by the volume of the aqueous phase in simulation box (in liter).

Figure 6.6b shows the orientational parameter \(\langle \cos \varphi \rangle\) of water in different simulation systems. First, it should be noted that although the value of \(\langle \cos \varphi \rangle\) in the gas phase (\(\Delta z < 0\)) looks significant, it does not convey any valuable information for this work. The reason is that the gas phase just accounts for a few vaporised water molecules whereas this work is focusing on the liquid water underneath the interface. Therefore, the gas phase region in Figure 6.6b is disregarded hereafter. Instead, the sub-surface region involving a layer of water underneath Gibbs dividing surface (GDS) is focused on. From Figure 6.6b, it is shown that pure water (blue circles) has neutral \(\langle \cos \varphi \rangle\) in the sub-surface region, indicating that the local water does not have any orientational preference. In contrast, all SDS solutions display a significantly negative \(\langle \cos \varphi \rangle\) in this region, which, by definition, indicates an aligned water layer underneath the GDS. Moreover, the interfacial
depth decreases from System A (≈ 35 Å) to Systems B (≈ 25 Å) to System C (≈ 15 Å), suggesting that the extent of water alignment decreases in the same sequence. In fact, the fluctuation of (cos φ) in System C may infer some perturbation to the alignment of water in this system.

These simulation results can be elucidated based on the distribution of DS− anions. First, the driving force of the water alignment is straightforward to understand. The surface adsorption of DS− anions also carries charges to the interface. The charged interface then induces an interfacial electrostatics field (IEF) which interacts with water dipoles and aligns them into a fashion that the water dipole vectors are favored to point towards the bulk water. Such alignment results in a negative (cos φ) as shown on Figure 6.6b. However, the alignment of water is perturbed by the dynamics of water itself and, especially, by the big DS− ions present in the sub-surface region. In particular, all of the DS− anions in System A were adsorbed onto methane-water interface, leaving the concentration of DS− in the bulk being negligibly small (see DS− profile on Figure 6.6a). The lack of DS− anion in sub-surface region gave no disturbance of water alignment, so that the water alignment was strongest in System A. In contrast, in Systems B and C, simulation results on Figure 6.7 show that only one portion of the initially inserted DS− anions was adsorbed onto methane-solution interface while the remaining part resided in the bulk. Specially, the formation of a stable micelle was observed in the bulk of system C (see Figure 6.7c). The presence of bulk-residing DS− anions, and especially the micelle, disturbed the alignment of water in Systems B and C, leading to a weakening of water alignment in these systems, as shown in Figure 6.6b. Because of this discussion, the condition of System A can be assigned to the sub-millimolar concentration in my experiments and the Systems B and C can reflect the high-concentration regime.

**Figure 6.7** Typical snapshots of methane-solution interface from my simulation. These are representative configurations of the equilibrium state of the interfaces. Only water and DS− anions are shown. The gas phase and Na+ cations are hidden for clarity. Panels (a), (b) and (c) are for the Systems A, B and C, respectively.
6.5 Effect of mixture of SDS and TBAB

In this section, I show how the effect of a mixture of SDS and TBAB is different from the individual effect of each surfactant. In Chapter 5, I showed that TBAB (tetra-butylammonium bromide) displayed a strong inhibition of CO₂ hydrate formation when it was used at the concentration of 3.6 mM. Thus, I used this concentration for the aim here. On Figure 6.8, the induction time of methane hydrate formation is shown along with the corresponding I(s)/I(w), for neat water, each single surfactant and mixed surfactants. The average induction time in neat water and 0.3 mM SDS solution was 7.35 (hour) and 20.44 (hour), respectively. In 3.6 mM TBAB solution, no sign of methane hydrate growth was observed after 24 hours of experiments. Even though, the induction time for this system was assigned to 24 hours for plotting purpose. Interestingly, the average induction time of methane hydrate formation in a mixture of 0.3 mM SDS and 3.6 mM TBAB was only 2.27 (hour), being much shorter than those in the solution of each surfactant. In the meantime, the value of I(s)/I(w) was smaller in the mixture than in the solutions of each surfactant. This result demonstrates that although both 0.3 mM SDS solution and 3.6 mM TBAB are strong inhibitors individually, the mixed solution of 0.3 mM SDS and 3.6 mM TBAB is an effective promoter.

![Figure 6.8 The effect of mixing surfactants on the induction time of methane hydrate formation and interfacial water alignment. Although both 0.3 mM SDS solution and 3.6 mM TBAB are strong inhibitors individually, the mixed solution of 0.3 mM SDS and 3.6 mM TBAB is an effective promoter. The ration I(s)/I(w) is smaller in the mixed surfactant solution compared to those in the solutions of single surfactant.](image)

---

67
6.6 General discussions

6.6.1 Correlation between water structure and hydrate kinetics

Using the magnitude of $I(s)/I(w)$ in SFG spectra as an indicator of water ordering at a gas-water interface [19, 20], I have identified two distinct configurations of interfacial water respectively at the surface of dilute and concentrated SDS solution. In low concentration, the presence of SDS induces an enhanced ordering of water at the solution surface and the greatest extent of water ordering is achieved at $C_{SDS} = 0.3$ mM. In higher concentration, a depression of water structure followed by a weakening of hydrogen bond network is evidenced through the downturn of $I(s)/I(w)$. Interestingly, this trend can be explained by simulation results. First, my simulations indicate that the ordering of water originates from the alignment of interfacial water under the effect of charged $DS^{-}$ absorbed on the interface. Secondly, the absence of $DS^{-}$ anions in the sub-surface of dilute SDS solution gives no disturbance of water aligning process, which could give a reasonable explanation to the strongest water ordering observed spectroscopically at $C_{SDS} = 0.3$ mM. Thirdly, the increasing presence of $DS^{-}$ anions and, especially, the micelles in the sub-surface of concentrated SDS solution perturbs the alignment of interfacial water (as observed in Systems C of the simulation), which could ultimately be responsible for the weakening of water ordering observed spectroscopically in the higher concentration.

Interestingly, the change in the structure of interfacial water has a strong correlation with the measured methane hydrate kinetics. Using the term $I(s)/I(w)$ to express the water alignment and the induction time to express methane hydrate kinetics, an intrinsic correlation between structural and kinetic properties is shown on Figure 6.9. Evidently, the strongest interfacial water alignment is observed together with the longest induction time at $C_{SDS} = 0.3$ mM. This observation should not be considered as a coincidence since a similar matching was also observed at $C_{TBAB} = 3.6$ mM CO$_2$ hydrate formation in TBAB solution in Chapter 5. Moreover, on Figure 6.8, it is shown that the correlation (stronger alignment-longer induction time) is also satisfied for methane hydrate formation in 3.6 mM TBAB solution. The evidence becomes more strengthened when it is being shown that a mixed solution of 0.3 mM SDS and 3.6 mM TBAB displays both a shortening of the induction time and a weakening of water alignment (see Figure 6.8). The weakening of the water alignment in this mixture is expected because the co-adsorption of two oppositely charged surfactants can lead to the neutralization of surface charge. Based on these results, I conclude that the alignment of water underneath surface adsorption of surfactants is the origin of the extraordinary inhibition of gas hydrate formation in dilute surfactant solutions.
Figure 6.9 The correlation between methane hydrate kinetics and interfacial water alignment in SDS solution. The data evidently show that a higher degree of interfacial water alignment results in slower hydrate formation kinetics.

6.6.2 Interfacial water alignment versus gas hydrate formability

I have evidently shown the water alignment at gas-solution interfaces being an inhibitor of gas hydrate formation. This is a freshly new finding. Here I discuss the physics underlying this. First, it is worth remembering that the formation of gas hydrate usually initiates at gas-water interface [22-25] where the local gas solubility is high enough to meet the required supersaturated condition for triggering the clathrate nucleation [26]. During the nucleation event, local water molecules (in the interfacial region) have to rearrange to accommodate the gas (methane) and conform to the presence of the guest. This process is also known as the hydrophobic hydration of gas. In certain conditions, the resulting hydrophobic hydration shells can further develop into hydrate cages, and then the cages build up hydrate crystals [26, 27].

Hence, the initially aligned water at the gas-water interface would create an unfavorable condition for the nucleation process. This is because, the nucleation of gas hydrates, as discussed above, requires a structural rearrangement of water molecules at the interface. Therefore, when interfacial water is aligned by an external field (e.g., the interfacial electrostatic field, IEF), the structural rearrangement becomes unfavorable as the driving force of nucleation has to surpass the electrostatic interaction between water dipoles and the field. The driving force of hydrate nucleation tends to rearrange water into clathrate-like conformation whereas the IEF inclines the water into aligned. Consequently, the nucleation of gas hydrate is hindered. Figure 6.10 illustrates the concept discussed here. Figure 6.10a shows the hydration of a methane molecule in ordinary water. In the snapshot, a water shell surrounding methane molecule with a hydrogen bond network is identified. This hydration shell can develop into a hydrate cage by transforming its structure and exchanging
water molecules with the bulk. In contrast, Figure 6.10b indicates an incomplete hydration of methane in aligned water in which the construction of the hydration shell is hindered due to the orientation of water molecules. This mechanism gives rise to the inhibition of gas hydrate formation in dilute SDS and TBAB solutions, as I have shown. Moreover, the inhibition though this mechanism is on the nucleation stage, explaining why the induction time is strongly affected by the surfactants.

Finally, it is noted that the promotion of methane hydrate formation in concentrated SDS solution is well-known in literature and, thus, is not focused on in this work. However, it is worth noting that such promotion does not conflict with the mechanism proposed above. Indeed, the weakening of water alignment in concentrated SDS solution is an expected observation, given the promotion being known in this concentration range. In the meantime, the presence of DS\(^{-}\) anions and its micelles in the sub-surface region can enhance the local solubility of methane [5, 28].

**Figure 6.10** The hydration of methane in ordinary water (a) and aligned water (b). The hydrogen bonds between water molecules on hydration shells are shown. The dark spheres with a negative sign on indicate the head group of surfactant. The surfactant-induced alignment of water results in an unfavourable condition for the hydration of methane (b).

### 6.7 Conclusion

I have employed a synergic combination of kinetics measurements, surface-specific SFG spectroscopy and molecular dynamics (MD) simulation to study, at a molecular scale, the effect of sodium dodecyl sulfate (SDS) on the formability of methane hydrate. Kinetic results show an extraordinary inhibition of the methane hydrate formation in SDS solution of sub-millimolar concentration (especially at \(C_{SDS} = 0.3 \text{ mM}\)), along with a well-known promotion effect in high
concentration regime. Moreover, I have established interesting evidence that the mixed solution of 0.3 mM SDS and 3.6 mM TBAB provides a good promoter despite the fact that the 3.6 mM TBAB solution itself is also an inhibitor. The results from SFG measurements and MD simulations show that the alignment of water underneath surface adsorption of surfactant ions gives rise to the inhibition effect. I have discussed this novel finding using the concept of energy barriers of the transformation of water structure at the interface during the nucleation of gas hydrates. The vanishing of the inhibition effect in the mixed surfactants solution is explained through the weakening of interfacial water alignment due to the neutralization of interface charge. This work, together with the results from Chapter 5, has shed light into a universal understanding of the effect of SDS and TBAB on gas hydrate formation.

References

Chapter 7

Interfacial Gas Enrichment and Structured Water at Hydrophobic Surface are the Origin of Gas Hydrate Promotion by Hydrophobic Solid Particles

Abstract

Hydrophobic solid surfaces have been found to promote the formation of gas hydrates effectively, and thus, help to realize the immense potential applications of hydrates in many sectors such as energy supply, gas storage and transportation, gas separation and CO$_2$ sequestration. Despite the well-known effectiveness, the molecular mechanism behind the promotion effect has not been thoroughly understood. In this work, I used both simulation and experimental means to gain insights into the microscopic level of the influence of hydrophobic solid surfaces on gas hydrate formation. On one hand, my simulation results show the presence of an interfacial gas enrichment (IGE) at hydrophobic surface and a gas depletion layer at hydrophilic surface. In the meantime, the analysis of water structure near hydrophobic solid interface based on the molecular trajectories also shows that water molecules tend to get locally structured near a hydrophobic surface while becoming depressed near a hydrophilic surface. On the other hand, the experimental results demonstrate the preferential formation of gas hydrate on a hydrophobic surface. The synergic combination of simulation and experimental results points out that the existence of an IGE and structured water network at hydrophobic solid surface plays a key role in promoting gas hydrate formation. This work advances the molecular level understanding of the role of hydrophobicity in governing the gas hydrate as well as interfacial phenomena in general.

---

Published in Journal of Physical Chemistry C 121 (2017) 3830-3840
7.1 Background context

Hydrophobic solid surfaces have been found to promote gas hydrate formation effectively. In particular, hydrophobic fumed silica powder is one of the best known hydrate promoters. It is an ultrafine silica powder with the surface being grafted with alkyl chains and, thus, is very hydrophobic [1]. In gas hydrate experiments, hydrophobic silica powder is mixed with water to a proportion of 1-5% (by weight) by using a high-speed blender to disperse water phase into miniscule drops which are fully covered by the powder [2-4]. The resulting mixture is apparently dry, free-blowing and usually called dry water [2-4]. Previous studies showed that dry water provides an excellent medium for accelerated formation of both carbon dioxide [5] and methane [2, 3, 6] hydrates. For example, it has been reported that methane uptake was increased from 3 (v/v) in ordinary water to 175 (v/v) in dry water, under the same experimental condition (v/v is the gas volume in STD condition per one hydrate volume) [2]. Shortened induction time (5-10 minutes) was also achieved in dry water system without agitation. In another work, the impact of surface hydrophobicity of silica sands on hydrate induction time was investigated [7]. It was found that hydrate induction time was decreased from 576 s in untreated (hydrophilic) sands to 71 s in treated (hydrophobic) sands [7]. Furthermore, hydrate induction time measurements were more reproducible with hydrophobic sands [7]. Besides these silica-based surfaces, many other hydrophobic surfaces such as activated carbon and metallic surfaces have been found to promote gas hydrate formation effectively.

Nonetheless, in contrast to such well-known promotion effects, the physics that governs the effects of hydrophobic surfaces is unclear and, in most cases, constructed based on assumptions rather than experimental evidence. For example, it is generally agreed that hydrophobic particles promote gas hydrate formation through a kinetic route by increasing interfacial area, which facilitates gas-water contact. However, it was also found that dry water shifted the equilibrium of methane hydrate to higher temperature and lower pressure [4]. This effect indicated that dry water acted as a thermodynamic promoter rather than a phase-contact facilitator. Moreover, it was also reported that hydrate formation was accelerated and became more deterministic (less stochastic) when the hydrophobicity of the solid surface was improved [7]. These findings are very interesting but they cannot be explained the available literature.

This chapter aims to gain deeper insights into the mechanism underpinning the promotion of gas hydrate formation by hydrophobic solid particles, particularly dry water. A special experiment was designed and implemented for examining the effect of surface hydrophobicity on the formability of CO₂ hydrate. Molecular dynamic simulation was employed to study local water
structure and local gas concentration near a hydrophobic surface and a hydrophilic surface. The findings of this work provide a universal explanation of the promotion effects of hydrophobic solid surfaces on gas hydrate formation regardless of the chemistry of the solid surfaces.

7.2 Simulation results

7.2.1 Simulation of solid-water interfaces

The method of simulation is described in Section 4.6.2. Figure 7.1 shows a typical example of the simulation systems used in this work. The interface between the solid and water is of particular interest. Two types of the interface were investigated: Hydrophobic solid-water interface and hydrophilic solid-water interface. Gas molecules (CH$_4$ and CO$_2$) were randomly inserted into the water phase in the initial configuration. The hydrophobic and hydrophilic solid surfaces are referred to as OTA and COO surfaces, respectively (see Section 4.6.2 for details about simulation method).

![Simulation system of solid-water interface](image)

**Figure 7.1** Simulation system of solid-water interface. A solid was in contact with water to form the interface. CH$_4$ molecules, for example, were inserted randomly in water phase to simulate dissolved methane.

7.2.2 Contact angle simulation

Simulation of contact angle is described in Section 4.6.3. Figure 7.2 shows the simulated contact angle of the water droplet on solid surfaces. For the OTA surface, water cluster retained its spherical shape with a contact angle being slightly fluctuating around its average value of 128° (the fluctuation is due to the dynamics of molecular system). This value is almost the same as the experimental value (130°) of water droplet on a hydrophobized glass surface, as shown on Figure 7.8a (Section 7.3.1). In contrast, water cluster on the COO surface spread out and eventually formed a water layer, resulting in a continual decrease in contact angle from an initial value of 145° to its equilibrium value of 0°. It is noted that the method of contact angle calculation described in Section 4.6.3 cannot be used to calculate the contact angle of either 0° or close to 0°. So, when the droplet on the COO surface had spread out virtually (the contact angle became small), VMD (Visual
Molecular Dynamics) software was used as an alternative mean to estimate the contact angle. From VMD, it could be seen that the water droplet transformed into a complete water layer after 1.5 ns, giving a contact angle of 0° which is the equilibrium value. The value of contact angle which was determined by using VMD is shown in dashed line on Figure 7.2. The simulation contact angle of COO surface (0°) agrees quite well with the experimental value of 5° for hydrophilized glass (see Figure 7.8a, Section 7.3.1). Thus, the OTA and COO surfaces will be referred to as hydrophobic surface and hydrophilic surface in the remaining part of this chapter.

![Figure 7.2](image)

**Figure 7.2** Simulation results for contact angle (θ) of a water droplet on a simulated hydrophobic (OTA) surface and hydrophilic (COO) surface. The equilibrium contact angles for the OTA and COO surfaces are 125° and 0°, respectively. The dashed line indicates the contact angle that was determined using the VMD software. The contact angle was assigned to 0° when the water droplet (on the COO surface) spread out completely, resulting in a water layer on the surface.

### 7.2.3 Density profiles of gas and water near a hydrophobic solid surface

Figure 7.3 shows the simulation results for the local molar density, \( \rho(\Delta z) \), as a function of the distance from the point of calculation to the hydrophobic solid surface, \( \Delta z \). The blue solid curve is the fitting of the computed water density by using tanh function in Eq. (7.1) in which the fitting parameters are \( a = 27.61, b = 0.4893 \) and \( c = 7.889 \) for the CH₄ system (Fig. 7.3a), and \( a = 27.60, b = 0.5533 \) and \( c = 3.299 \) for the CO₂ system (Fig. 7.3b).

\[
\rho_w(\Delta z) = a\{1 + \tanh[b(\Delta z - c)]\}
\]  

(7.1)

From the density profiles, it is seen that there is a substantial reduction in water density in the interfacial region (within 12 Å from the interface for CH₄ system and 7 Å for CO₂ system). Beyond those distances, \( \rho_w(\Delta z) \) approaches a constant value of around 55.5 M (or 1000 g/L) which is the
correct density of bulk liquid water. Compared to the density profile of water at a vapour-water 
interface [8, 9], the computed density profile of water at the hydrophobic-water interface shares a 
similar pattern. Indeed, this similarity is expected, and it reinforces the credibility of the results as 
the hydrophobic solid-water interface has been previously proven to behave like a gas (vapour)-
water interface [10].

In contrast to the case of water, the density profiles of gases (CH$_4$ and CO$_2$) show a strong 
enrichment of the gas density in the interfacial region. Consider the case of CH$_4$ in Figure 7.3a, for 
example, the gas-enriched zone extends to the distance of 12 Å from the hydrophobic surface of 
of which the first 4 Å layer adjacent to the interface has no water ($\rho_w(\Delta z) = 0$). This observation 
indicates that methane fully occupies an interfacial layer of 4 Å from the hydrophobic surface and 
completely expels water from this region, forming a complete dense gas layer (DGL) covering 
the hydrophobic surface entirely. Indeed, it is worth noting here that previous data from both 
experimental techniques (e.g., Atomic Force Microscopy [11]) and computer simulation [12] ha 
also suggested the existence of nitrogen gas layer on a graphite surface. Even though, my finding 
here is still very interesting because it not only provides a further proof of the existence of DGL but, 
as the current focus is on an alkyl-grafted surface, it also opens a new way to understand and 
explain the gas hydrate phenomenon which will be discussed in the later sections.

However, in the next layer (4 Å ≤ $\Delta z$ ≤ 12Å), CH$_4$ density decreases gradually while water 
density increases rapidly. Actually, this layer is a mixture of methane and water in which local mole 
fraction of CH$_4$ is very high. By integrating the density profiles, the mole fraction of CH$_4$ in this 
layer is calculated to be around 0.14. Compared to the typical mole fraction of a light hydrocarbon 
of 0.15 at vapour-water interface [13], the calculated value is highly comparable. In the region 
beyond 12 Å from the hydrophobic surface, the concentration of methane slightly fluctuates at its 
average value of 0.19 M while the density of water levels off at 55.5 (M) (or 1000 g/L), which 
indicates the bulk condition being reached.

In Figure 7.3b, the density profiles of CO$_2$ and water are shown. In general, the density 
profiles of CO$_2$ system share similar features with those of CH$_4$ system, except the point that there 
is no dense gas layer observed for CO$_2$. Indeed, the density of water in the first layer adjacent to the 
solid surface is not equal to zero like in the case of CH$_4$. To understand this difference, we should 
consider the difference in induced dipoles between CO$_2$ and CH$_4$. For example, the C=O bonds in 
CO$_2$ are more polarisable than the C─H bonds in CH$_4$. Such features of CO$_2$ molecule make it less 
hydrophobic compared to CH$_4$. Indeed, carbon dioxide is a weak acidic gas which can interact 
chemically with water and dissociate slightly in water whereas methane is absolutely chemically
inert to water in the condition of gas hydrate formation. In another words, carbon dioxide does not have an adequate driving force of hydrophobic assembly to expel all water out of the interfacial region.

**Figure 7.3** Density profiles of gas and water near a hydrophobic solid surface: (a) CH₄ system and (b) CO₂ system. The blue solid curves are the fitting of water density using tanh function. These is a similarity between these two gases except no evidence of a gas dense layer for CO₂. The initial concentration of gas (both CH₄ and CO₂) is 1.39 M or 210 gas molecules per 5400 water molecules. For clarity, the constant density profiles beyond 18Å of Δz are not shown.

### 7.2.4 Density profiles of gas and water near a hydrophilic solid surface

**Figure 7.4** Density profiles of gas and water near hydrophilic solid surface: (a) CH₄ system and (b) CO₂ system. The formation of a hydration layer at a hydrophilic surface is evidenced. Gas is expelled from a hydrophilic surface as shown by a narrow depletion in the gas density profile.

Figure 7.4 shows the density profiles of gas (CH₄ and CO₂) and water near a hydrophilic solid surface. In general, the density profiles here are opposite to those in the case of hydrophobic solid surface. First, it is seen that there is a significant increase in the density of water adjacent to a hydrophilic surface. The maximal concentration of water of around 87 M (an increase of about 60% compared to that in the bulk) is achieved at the distance of Δz = 1.8 Å. This locally high density
can be assigned to the formation of a complete hydration layer at the hydrophilic surface. In the meantime, gas molecules are expelled from the hydration layer, resulting in a narrow depletion in the gas density at the interface, as clearly seen on the insets of Figures 7.4a,b.

7.2.5 Local water structure near solid surfaces

Recent experimental studies based on Raman spectra indicated that water molecules get more ice-like ordered in the vicinity of a hydrophobic surface (in contrast to the bulk water and near a hydrophilic surface) which change can accelerate the hydrate formation [14]. However, the detailed microscopic picture of the change in water local structure was not accessible by such experiment. Here, I have analysed my molecular dynamics trajectories to investigate how the hydrophobic surface influences the local structural order of the water adjacent to it. To quantify the extent of ordering in the local structure of water, a suitable order parameter is needed. The most common order parameter used to probe the "ice-like" structure is the tetrahedral order parameter $q_4$ [15]. The tetrahedral order parameter $q_4$ is defined by Eq. (7.2) [15].

$$q_4(i,t) = 1 - \frac{3}{8} \sum_{j=1}^{3} \sum_{k=\{j+1\}}^{4} \left( \frac{1}{3} + \cos \beta_{jk}(i,t) \right)^2$$  

(7.2)

where $\beta_{jk}(i,t)$ is the angle among oxygen atoms $j, i$ and $k$ at time $t$; $j$ and $k$ are the 4 nearest-neighbor oxygen atoms of the $i^{th}$ oxygen atom. Then a value of $q_4 = 1$ indicates that water molecule $i$ has a perfect tetrahedral structure, and a lower value indicates the nontetrahedral structure. Since I was interested to investigate how the water molecules near the solid-water interface are influenced by the surface, it is necessary to define the water molecules based on their distance from the interface. Usually the conventional interface is defined at the position where water density becomes half of the bulk (e.g., the conventional interface is at $\Delta z = 8$ and $\Delta z = 3.5$ in Figure 7.3a and 7.3b, respectively). However, at molecular scale, a mean (unchanged) interface over a complete simulation period might be confusing; rather, an instantaneous interface should be used [16]. An instantaneous interface considers the dynamic properties of water at the interface. Here I have calculated the instantaneous interface as defined by Willard and Chandler [16] to determine water density as a function of the distance from the instantaneous interface. For the hydrophobic solid-water interface, the density oscillation has two clear maxima (see Section 11.3.3, Appendix). This is consistent with what was observed for the air-water interface in previously reported simulations [16]. I have considered the distance of the first maximum as the first layer (called Interface region 1) and the distance of second maximum as the second layer (Interface region 2) of interfacial waters. In contrast to hydrophobic solid-water interface, the hydrophilic
solid-water interface has only one interfacial region as depicted by one maximum (see Section 11.3.3, Appendix).

Now I use the order parameter $q_4$ to analyze the local water structure at the interfacial region and in the bulk phase. However, it should be noted that the calculation of $q_4$ from Eq. (7.2) assumes that each water molecule has other four coordinated waters. Unfortunately, the water molecules at the interfacial region might not have the same coordination number or the same number of hydrogen bonds as in the bulk, which can create artifacts in the calculations of $q_4$. Because of this reason, I have calculated the coordination numbers and hydrogen bonds (HBs) for water molecules at the interface and in the bulk, for both hydrophobic surface and hydrophilic surface. Figure 7.5 shows the obtained results. It is shown that in interfacial region more water molecules form three-coordinated first solvation shell and two or three hydrogen bonds with the nearest neighbours. This data indicates the tendency of the decrease in both coordination number and hydrogen bonds of interfacial water.

**Figure 7.5** Probability density distribution of the coordination number (a, c) and hydrogen bonds (b, d) formed by a water molecule at the interface and the bulk. Some terminologies are self-explained in the figures. Probability density are not normalised to the density of water molecules for the bulk and the interface. Coordination number was defined as the number of water molecules found within 3.2 Å of the central water molecule. Hydrogen bond was defined by the distance and angle criteria (O–O distance of 3.45 Å and O_d–H–O_a angle of 30°).
The \( q_4 \) value for a three-coordinated water molecule will be different from that of a four-coordinated water molecule. It will be therefore more meaningful to compare \( q_3 \) and \( q_4 \) separately for the three- and four-coordinated water molecules, respectively. The \( q_3 \) is defined as the similar way as \( q_4 \) is defined, but only considering first three nearest-neighbour water molecules instead of four. As shown on Figure 7.6a, the water molecules at the hydrophobic solid-water interface having three coordinated waters within 3.2 Å preserve almost the same degree of tetrahedrality (in terms of \( q_3 \)) as those in the bulk. For the four-coordinated water molecules (see Figure 7.6b), interfacial waters are slightly less tetrahedral than those in the bulk. Since I have demonstrated that water molecules at the interface have less tendency to form four-coordinated sphere compared to in the bulk, and the change in the tetrahedrality (\( q_4 \)) is so small, I conclude that in terms of tetrahedrality order parameters \( q_3 \) and \( q_4 \), water structure next to a hydrophobic solid surface remains almost similar as in the bulk region.

The \( q_4 \) order parameter only considers the arrangement of the water molecules in the first solvation shell. However, the change in the local water structure might happen in the interfacial region between the first and second solvation shells which need to be considered by a separate order parameter. The distance between the fourth and fifth nearest neighbours is a suitable order parameter to probe that. This order parameter has recently been used to probe the change in the local structure of water when subject to cooling [17]. Since the coordination numbers of the water molecules change in the interfacial region, like the \( q_3 \) and \( q_4 \) order parameters, I have calculated two other order parameters \( d_{34} \) and \( d_{45} \). The radial distance between the third and fourth nearest neighbours for the water molecule having a coordination number of three was termed as \( d_{34} \), and the radial distance between the fourth and fifth nearest neighbours for the water molecule having a coordination number of four was termed as \( d_{45} \). As shown in Figure 7.6c and 7.6d, in the first interfacial region (Interface region 1) near the hydrophobic surface, the water molecules have the tendency to achieve a higher value of \( d_{34} \) and \( d_{45} \), which indicates an increase in the separation between the first and second solvation shells, manifesting a more structured local water. This result is consistent to the work of Malaspina et al. [18] who found the structural ordering of the water molecules near a graphene-like hydrophobic surface in terms of local structure index (LSI) order parameter.
Figure 7.6 Probability density distribution of the tetrahedrality order parameter $q_3$ and $q_4$ (a, b), and $d_{34}$ and $d_{45}$ (c, d) for water molecules at the interface and in the bulk for the hydrophobic surface with water. Interface region 1 encompasses the region within 3.2 Å from the instantaneous interface. Likewise, Interface region 2 is between 3.2 Å and 5.5 Å. The bulk is beyond the distance 5.5 Å. Probability densities are not normalised to the density of water molecules for the bulk and the interface.

Figure 7.7 shows a similar set of data, but for the hydrophilic solid-water interface. Compared to the water molecules in the bulk, the distribution of probability density of interfacial region substantially shifts left (toward lower values of $q_3$ and $q_4$, respectively). This change provides a concrete evidence of a depressed water structure in the interface region near a hydrophilic surface. On the basis of these results, it is thus concluded that the water molecules in the interfacial region of a hydrophobic solid-water interface have the same degree of tetrahedrality as the bulk water (in terms of $q_3$ and $q_4$) or become more structured than the bulk water (in terms of $d_{34}$ and $d_{45}$). In contrast, the water molecules at the hydrophilic solid-water interface have a clear decrease in the tetrahedrality in terms $q_3$ and $q_4$ order parameters.
Figure 7.7 Probability density distribution of the tetrahedrality order parameter $q_3$ (a) and $q_4$ (b) for water molecules at the interface and in the bulk for the hydrophilic surface with water. Interface region 1 encompasses the region within 3.2 Å from the instantaneous interface. Likewise, Interface region 2 is between 3.2 Å and 5.5 Å. The bulk is beyond the distance 5.5 Å. Probability densities are not normalised to the density of water molecules for the bulk and the interface.

7.3 Experimental results

7.3.1 Gas hydrate formation at hydrophobic surface

It would be noted that previous works have shown promoting effects of hydrophobic surfaces on both CO$_2$ [3, 5] and CH$_4$ [2-4] hydrate formation. Given this known fact, the aim of the experiment part in this work is to show such effect in a visual way. The visualization of the phenomenon is exemplified for CO$_2$ hydrate since, in general, CO$_2$ hydrate requires a lower operation pressure (compared to the case of CH$_4$ hydrate) and, therefore, is suitable for my experiment system. The experimental setup and procedure are described in Section 4.3, Chapter 4.

Figure 7.8 shows the influence of hydrophobicity of solid surfaces on the formation of CO$_2$ hydrate. Two different modified glass surfaces with the water contact angles of 130° and 5° are shown on the left images (Figure 7.8a). The solid surfaces were in contact with water (see Section 4.3, Chapter 4). In this experiment, quiescent condition was applied. As can be seen from Figure 7.8a, the interfaces between water and the two modified glass surfaces were apparently similar prior to pressurization. When the reactor was pressurized with CO$_2$, gas hydrate initiated at three-phase (gas-liquid-hydrophobic solid) contact line and developed slowly along the direction of the hydrophobic solid-water interface (Figures 7.8b,c). At 12 hours after pressurization, CO$_2$ hydrate crystals were clearly observed on the hydrophobized glass surface. However, no hydrate formation was observed on the hydrophilic surface.

In a similar manner, Figure 7.9 shows the shape of the CO$_2$ hydrate formed under the agitated condition. In this case, the gas hydrate also preferentially formed on the hydrophobized glass
surface like the case of quiescent condition. However, as stirring condition was applied, hydrate crystals could initiate on the hydrophobic solid surface submerged in water (i.e. unnecessary at the three-phase contact line as in the case of quiescent system) and developed into big crystals, as shown on Figure 7.9. In combination with data from Figure 7.8, it is figured out that CO\textsubscript{2} hydrate formed preferentially on the hydrophobic surface regardless of the availability of agitation condition. This finding is crucially important for understanding the role of hydrophobic solid particles in governing gas hydrate formation, which will be discussed further in the later sections.

<table>
<thead>
<tr>
<th>Before pressurization</th>
<th>1 hour after pressurization</th>
<th>12 hours after pressurization</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="before.png" alt="Image" /></td>
<td><img src="after1.png" alt="Image" /></td>
<td><img src="after2.png" alt="Image" /></td>
</tr>
</tbody>
</table>

**Figure 7.8** The preferential formation of CO\textsubscript{2} hydrate on the hydrophobic surface under quiescent condition. (a) shows the image of the solid-water interfaces before pressurization; the insets show the contact angles of water droplets on the modified solid surfaces. (b) shows the interfaces after 1 h of pressurization. (c) shows the interfaces after 12 h of pressurization: a hydrate crystal was formed on the hydrophobic surface but no hydrate was observed on the hydrophilic surface. Experiments were conducted at 6 MPa and 1\textdegreeC

![Image](bubble.png)

**Figure 7.9** Preferential formation of CO\textsubscript{2} hydrate on a hydrophobic surface under stirring of water.

7.3.2 *Bubble formation on hydrophobic and hydrophilic surfaces*

This section is to show further evidence of high gas density at hydrophobic solid-water interface. The experimental setup was similar to the setup of gas hydrate formation (described in
Section 4.3). A see-through high-pressure reactor with two modified glass surfaces installed inside was pressurized to 4 MPa at ambient temperature (25°C). At this condition, CO₂ hydrate could not form. This condition was kept for 2 h for attaining the equilibrium of gas dissolution into water. Then reactor was slowly depressurized (pressure dropped by 0.2 MPa per minutes) to observe gas bubble formation on the glass surfaces.

Figure 7.10 Formation of CO₂ gas bubbles on a hydrophobic surface (left) and on a hydrophilic surface (right). On the hydrophobic surface, gas bubbles nucleate and grow very intensively but there are only a few bubbles formed slowly on the hydrophilic surface.

The results are shown in Figure 7.10. During the process of depressurization, gas bubbles nucleated and grew very actively on the hydrophobic surface. When the bubbles reached a certain size, they buoyed up and new bubbles were formed. In contrast to the hydrophobic surface, there were only a few bubbles that occasionally formed and developed slowly on the hydrophilic surface. This observation demonstrates the existence of high gas density at the hydrophobic surface which could supply an adequate amount of gas for bubble nucleation and growth. Furthermore, because gas molecules could contact the hydrophobic surface as per the simulation results, heterogeneous nucleation of gas bubbles could occur on the hydrophobic surface. Compared to homogeneous nucleation, heterogeneous nucleation could take place more favourably, resulting in the intensive formation of gas bubbles at the hydrophobic surface as observed. This experimental observation also agrees well with theoretical results about gas bubble nucleation at the hydrophobic vicinity by Zhou et al [19]. In contrast to the hydrophobic surface, as discussed in the simulation section, a complete hydration layer existed on the hydrophilic surface which prevented gas from contacting the surface and therefore preventing heterogeneous nucleation of gas bubbles. Thus, it is concluded that the high gas density and heterogeneous nucleation were responsible for the preferential formation of gas bubbles at the hydrophobic surface. In a cooperative way, this experimental observation supports the simulation finding of interfacial gas enrichment at a hydrophobic surface.
7.4 General discussion

Wang et al. [7] showed that sands hydrophobized with interfacial alkyl-grafted layer could foster the formation of methane gas hydrate, and the formation kinetics increased with the increase in the surface hydrophobicity of sand particles. In this work, I conducted the simultaneous experiments on both hydrophobic and hydrophilic surfaces and was able to show the significant effect of surface hydrophobicity on gas hydrate formation. I could differentiate, in a direct and visual way, the difference between hydrophobic and hydrophilic surfaces in affecting gas hydrate formation. The current finding of the preferential formation of CO$_2$ gas hydrate on a hydrophobic surface provides further rigorous evidence of the critical role of hydrophobicity in gas hydrate formation.

Before discussing such role of hydrophobic surfaces on the formation of gas hydrate, I briefly review the molecular pathway of gas hydrate formation in neat water. Fundamentally, gas hydrate formation is a successive transformation of water structure from an initial liquid state into an ice-like (solid) state during which gas molecules (the hydrate formers) are trapped in the cavities of the ice-like solid. In the structure I of gas hydrate (of which CH$_4$ and CO$_2$ can form), the ideal mole fraction of gas is 1/6.75 (equivalent to 1 mole of gas per 5.75 moles of water) [13]. The practical mole fraction of gas in real gas hydrate is slightly lower due to the incomplete cage occupancy. However, the solubility of hydrate formers in bulk water is typically of several molecules per thousands of water molecules [13], which is too small to provide a thermodynamic driving force sufficient for initiating the formation of gas hydrate by nucleation. Consequently, bulk nucleation of gas hydrate is normally difficult. Alternatively, interfacial nucleation of gas hydrate is frequently observed [20-23] because the local mole fraction of hydrate formers at the gas-water interface can be very high [13]. This fact (that gas hydrate can only nucleate at the gas-water interface) results in two enduring kinetic problems. First, interfacial molecules, both water and the guests that involve directly in gas hydrate formation, just account for a very small portion of the total system. In other words, the majority of molecules that stay in the bulk are not involved in the formation process. Secondly, as hydrate forms at the interface, it forms a hard solid layer which isolates the water phase from the vapour phase, which in turn diminishes the formation kinetics. Due to these two problems, gas hydrate formation in neat water, especially in the case without agitation, is slow and incomplete.

However, when hydrophobic particles are present, the fashion of gas hydrate formation can be changed kinetically and thermodynamically. In terms of kinetics, my simulation results show that when solid particles are added to the hydrate-forming system, the local concentration of hydrate
formers at the solid-water interface is either enriched or depleted, depending on the solid surface being hydrophobic or hydrophilic (as schematically illustrated on Figure 7.11), respectively. The locally-high density of hydrate formers at hydrophobic solid surfaces provides an excellent condition for gas hydrate formation, similar to the gas-water interface. In other words, instead of nucleating at the gas-water interface only as for the gas-neat water system, the nucleation of gas hydrate in hydrophobic solid-containing systems can take place on the hydrophobic solid-water interface whose total area would be much larger than the gas-water interface itself. High local gas density and large space for (heterogeneous) nucleation to take place are the facts accounting for the gas hydrate-promoting behaviour of hydrophobic solid particles. This argument is strongly supported by and also gives reasonable explanation for experimental observation that when hydrophobic solid particles were added, gas hydrate could nucleate and grow rapidly in the whole aqueous system (rather than at gas-water interface only as in the case of neat water), even without agitation [2, 3].

Figure 7.11 Graphical illustration of gas density profile at the interfacial regions of the hydrophobic solid-water and hydrophilic solid-water interfaces, in comparison with those in the bulk. The interfacial gas enrichment at a hydrophobic surface is attributed to the origin of gas hydrate promotion by hydrophobic solid particles.

In the term of thermodynamics, the analysis of molecular trajectories also points out the distinct difference between water structure near hydrophobic and hydrophilic surfaces. While water molecules at hydrophobic solid-water interface have a tendency of increasing the tetrahedrality of the local structure, the water molecules at hydrophilic solid-water interface are shown with a depressed structure. In addition to the opposition in attracting gas molecules to the interface, this difference in structural properties gives reasonable explanations to the opposition in affecting gas hydrate formation of hydrophobic and hydrophilic solid surfaces (the hydrophobic surface can promote gas hydrate formation whereas the hydrophilic surface cannot).
7.5 Conclusion

I studied the effect of surface hydrophobicity on the properties of solid-water interfaces and its connection to hydrate formation, using both molecular dynamics simulation and experimental means. On one hand, the simulation results show the influence of surface hydrophobicity on the locally elevated density of gases (hydrate formers) as well as on the local ordering of water near a hydrophobic solid surface. On the other hand, the experiments provide a direct observation of the preferential formation of gas hydrate on a hydrophobic solid surface. The combination of simulation and experimental results demonstrates that the existence of interfacial gas enrichment (IGE) and the tendency of getting more locally structured of water both at hydrophobic surfaces give rise to the promotion of gas hydrate formation in hydrophobic particles-containing systems. The outcome of this work advances our knowledge of interfacial science. In particular, it helps developing a better understanding, at a molecular scale, of the mechanism of gas hydrate promotion by hydrophobic solid particles.

References


Chapter 8

The Dual Effect of Sodium Halides on the Formation of Methane Hydrate

Abstract

Inorganic salts are known to inhibit the formation of gas hydrates. Here I show the duality of sodium halides of submolar concentration in affecting the formation of methane gas hydrates. Sodium halides, especially NaI, at low concentration effectively promote methane hydrate formation while they all turn to be an inhibitor at high concentration. Maximum gas consumption, growth rate and induction time were experimentally determined as a function of salt type and concentration. I explain the dual effect of salts by the hydrophobic hydration. The promoting effect of dilute sodium halides is due to the fact that large and polarizable anions (e.g., iodide) behave as hydrophobic entities and interact with surrounding water molecules to form hydrophobic hydration shells whose water structure is similar to that of hydrophobic hydration shells of methane. Since hydrophobic hydration of methane in neat water is thermodynamically unfavourable because it associates with a negative entropy change and a partial loss in the hydrogen-bonded network, the structurally similar shells of halide ions facilitate the process of entropy change and, therefore, facilitate gas hydrate nucleation. This proposal also explains the decrease in the promoting capability of salts in the order from iodide to fluoride because of the decrease in hydrophobicity of the halide ions. The inhibition effect of salts at high concentration is explained by the advantageous competition of the halide ions with methane gas molecules to gain water for hydration as well as their radical effect on distorting the water structure. This hypothesis is experimentally supported by the difference in the salt recovery into hydrates and the hydrophobicity (measured by contact angle) of halide ions. Nonetheless, further research is required to obtain a fuller insight into the influence of salts and additives on gas hydrate formation.

---

4 Published in Fuel 156 (2015) 87-95
8.1 Background context

Besides surfactants and hydrophobic solid particles, salts are important additives to gas hydrate formation. They are ubiquitous in gas hydrate systems. For example, marine environments where natural gas hydrates exist are abundant with salts. Fluids which are transported through subsea pipelines also contain some trace amount of salts. Salts are also unintentionally added to hydrate systems through processing water, the used chemicals or even as a product from the corrosion of equipment. Therefore, the presence of salts (or more strictly saying, of ions) in hydrate systems is unavoidable. In terms of science, the relation between ions and gas hydrate formation can be interesting. Ions are well known to disrupt water structure strongly [1] and, therefore, they can be an effective thermodynamic inhibitor for gas hydrate formation [2-4].

However, it was recently shown that sodium halides at low concentrations promote the formation of CO$_2$ hydrate [5]. Therefore, salts are not an inhibitor only (as widely known) but can also be a promoter in low concentrations. Moreover, besides carbon dioxide, methane is also the most common gas hydrate former. However, methane is different from carbon dioxide in that methane does not dissociate in water whereas carbon dioxide can partially dissociate in water, lowering the solution pH slightly. Hence, it is important to know whether the gas hydrates of these two guests share the same salt-dependent patterns. More importantly, previous research mostly focused on experimental measurement of macroscopic kinetic parameters and left the microscopic mechanism unanswered. While the inhibition of gas hydrate formation by concentrated saline solutions is attributed to the reduction in gas solubility, increase in viscosity, water-gaining competition between ions and guests as well as the disruption of water structure by ions [6], the mechanism of the hydrate promotion by dilute sodium halides solutions has not been understood.

This work aims to investigate the influence of sodium halides, of submolar concentrations (0 to 1000 mM), on the formation of methane hydrate and provide an explanation for the experimental observation. Indeed, the findings of this chapter provide a conclusive understanding of the influence of sodium halides on methane hydrate formation. More importantly, I show here for the first time the ion-specific effect on gas enclathration. Together with previous chapters which have shown important new insights into the effects of surfactants and hydrophobic solid surfaces on gas hydrate formation, this chapter provides deeper insights into the effects of inorganic salts, an important sort of gas hydrate additives.
8.2 Effect of sodium halides on methane hydrate formation

8.2.1 Gas pressure and temperature versus time: T-P graphs

Figure 8.1 Pressure (solid lines) and temperature (dashed lines) versus time during methane hydrate formation in sodium iodide solutions of different concentrations. The pressure and temperature at zero time were 1465 psi (10 MPa) and 24-25 °C, respectively. The target temperature was set to be 1.5°C.

Figure 8.1 shows the typical results obtained with NaI solutions for the change in gas pressure and temperature versus time. For the first ten minutes, there was a sudden drop in both the temperature and pressure due to the cooling of the system being immersed into the cooling bath. The drop in pressure was induced by the gas contraction and dissolution into the liquid phase. The induction period was then followed. During this period, the temperature of system remained fairly constant at around 1.5°C while the pressure continued decreasing, indicating that methane continued dissolving into liquid phase to create a supersaturated solution needed for the initiation of gas hydrate formation. The induction period lasted for a few minutes to hours, depending on the salt concentration. Subsequently, the pressure still continued decreasing but the temperature started rising rapidly to about 5 – 7 °C and stayed at this temperature for about one hour even the cooling bath kept cooling the system to the target temperature. This increase in temperature is assigned to the exothermal formation of gas hydrates and indicates the onset of gas hydrate formation. After some time, the gas hydrate formation diminished and completed as evidenced by the sudden drop in
temperature to a constant value and the stabilization of pressure at a constant level. The changes in gas pressure and temperature with NaBr, NaCl and NaF solutions share the same trend. Thus, I only show here the T-P graphs of the experiments with NaI solutions.

8.2.2 Methane consumption versus time

The change in gas pressure and temperature versus time was converted into the gas consumption using Eq. (4.1) in Chapter 4. Figure 8.2 shows the gas consumption versus time of methane hydrate formation in sodium halides solutions of different concentrations. For the concentrations examined, the change in gas consumption with time follows a similar increasing trend. The rapid increase for the first ten minutes was due to the dissolution of gas because of cooling as shown previously in Figure 8.1. This increase in gas consumption for this period was independent of salt type, possibly because of the low salt concentrations used in the experiments, creating no discernible effect in gas solubility [7, 8].

![Graphs showing methane consumption over time for NaI, NaBr, NaCl, and NaF solutions.](image)

**Figure 8.2** Effect on sodium halides and their concentration on methane consumption versus time. The water line divides the curves into two groups, showing the dual effect of sodium halides on the formation of methane gas hydrate: sodium halides promote gas hydrate formation at low concentration whereas they become an inhibitor at higher concentration.
After the first ten minutes, the gas consumption started increasing due to gas hydrate formation and became salt-dependent. The curve for neat water (blue) divides the gas consumption curves into two groups, one group of curves for very dilute salt concentrations over it and another group of curves for high salt concentrations below it. The transition salt concentration was 50-75 mM. The dilute salt solutions promoted hydrate formation while concentration higher than the transition concentration inhibited hydrate formation. For example, 50 mM NaI solution increased the gas consumption by about 20% compared to neat water. However, concentrated salt solutions such as 250 mM NaF solution and 1000 mM solutions of NaI, NaBr or NaCl significantly reduced the gas consumption. Furthermore, no significant rise in temperature was observed for these cases because the associating slow kinetics produced no significant amount of heat exceeding the heat transfer efficiency of the system. It noted that as a 250 mM NaF solution was found to virtually inhibit gas enclathration and, therefore, no higher concentrations of NaF was investigated.

8.2.3 The rate of hydrate growth

Growth rate provides explicit information on gas hydrate kinetics and, therefore, is indicative to the influence of salts. The rate of hydrate growth in different salt solutions at different concentrations was calculated using Eq. (4.2) in Chapter 4. Figure 8.3 shows the calculated rate versus time. The growth rate for the first 10-20 minutes is not related to gas hydrate formation and is not shown in Figure 8.3.

![Figure 8.3](image)

Figure 8.3 Effect of sodium halides and concentration on growth rate of methane hydrate versus time. The blue line for water is shown as a reference.

As shown in the left graph of Figure 8.3, the rate of hydrate growth in individual solutions of low salt concentration (75 mM) reaches a peak at a specific time which corresponds to the sudden rise in temperature as exemplified in Figure 8.1 for NaI. Evidently, this significant hydrate growth indicates the onset of gas hydrate formation. Approximately, the next one hour is the gas hydrate
formation period as evidenced by both the temperature rise (see Figure 8.1) and moderate growth rate. Then, the growth rate eventually decreased to zero (and the temperature approached a constant value – see Figure 8.1), indicating that gas hydrate formation finished. The peak of the growth in water occurred later than the peaks of the growth in the dilute salt solutions.

The right graph of Figure 8.3 shows the hydrate growth rate in high salt concentration solutions. Evidently, the growth rate significantly decreased in the concentrated salt solutions. The peaks of the growth rate in all solutions are below the peak of the growth rate in water. The peaks of the growth rate in the 1000 mM NaI and NaBr solutions are shifted to the end, indicating not only slow growth rate but also long induction time as discussed in the next paragraph. In the 1000 mM NaCl and 250 mM NaF solutions, no apparent peaks on the growth rate (and on temperature, not shown) curves are observed, explicitly indicating that methane hydrate formation in these two solutions was virtually inhibited. A reduction in gas consumption by approximately 50% in comparison with water was also identified with the two solutions (Figure 8.2).

**8.2.4 The induction time**

Theoretically, induction time is the period of time between the creation of supersaturated solution and the occurrence of first crystals of gas hydrate. It is, however, practically difficult to quantify induction time defined in this way. Here, I define the induction time as the time interval between the beginning of each experiment and the point of time at which the growth rate peaked. This definition is practically applicable and provides a good approximation for comparing the effect of salts on the kinetics of gas hydrate formation. Interestingly, it is seen on Figure 8.3 that the induction time of methane hydrate formation in 75 mM salt solutions was shorter than that in water. In particular, 75 mM NaI solution significantly reduced the induction time of methane hydrate formation.

Figure 8.4 shows the experimental results for the maximum gas consumption and induction time. Evidently, with increasing salt concentration, the gas consumption by the hydrate formation first increased, reaching a maximum at 50-75 mM and then decreased. The effect of the dilute NaI solution on the gas consumption was the most significant, while the effect of NaF solutions on increasing the gas consumption was the weakest. The trend of the change in induction time with increasing salt concentration was reverse to the trend of the gas consumption. In case of no peak appearing on the growth rate curve, the corresponding induction time was extremely long and, therefore, was described as infinity.
Figure 8.4 Dependence of maximum gas consumption (top) and induction time (bottom) on sodium halides and their concentrations. The induction times at high concentrations of NaCl and NaF are extremely (infinitely) long.

8.3 Discussion about the effect of sodium halides

8.3.1 The dual effect of sodium halides on gas hydrate formation

The experimental results for both the growth rate and induction time show that the halide salts display a dual effect on methane hydrate formation. At low concentration, the halides promote the hydrate formation, while at high concentration they act as inhibitors. The transition concentration is around 50-75 mM. The results also show that not only salt concentration is critical to the hydrate formation but also the type of halide anions can significantly impact the hydrate formation. The promoting capability decreases in the order NaI, NaCl ≈ NaBr, NaF. Thus, the radius, polarizability and charge density of halide ions are the determining factors of promoting capability of sodium halides. The larger and more polarizable halide ions are the greater promoting capability they can display.

The dual effect of salts on hydrate formation is of both scientific and practical importance. It contributes to a comprehensive understanding of the effect of salts on the formation of gas hydrates since the conventional standpoint considers salts as gas hydrate inhibitors only. A misunderstanding
of the promoting behaviour of dilute salt solutions may be serious since we may thus underestimate the correspondingly potential risks. For example, fluids inside submarine pipelines often contain small content of salts (sodium chloride and magnesium chloride) and underestimating the effect of their presence may cause catastrophic problems. For example, the explosion of BP’s rig in the Gulf of Mexico in 2010 was attributed to the blockage of pipelines caused by gas hydrate formation [9].

Understanding the microscopic conceptual picture of the salt effect is a challenging but fascinating task. The extraordinary properties of sub-molar concentration salt solutions have increasingly attracted research interests in several fields and have been intensively investigated thanks to the advancement in instrumental techniques and theoretical approaches. Many ongoing efforts reveal anomalous behaviours of dilute sodium halide solutions at a microscopic scale and, thereafter, linking them to many macroscopic observations is rewarding. However, there still remain many mysteries about sub-molar solutions and motivates researchers in many disciplines. For instance, as the salts influence gas hydrate kinetics in many aspects such as changing the induction time, the growth rate and the gas consumption, they must change the fashion of both gas hydrate nucleation and growth. In the following sections, I attempt to provide and argue possible explanations for my result via linking some extraordinary properties of halide ions, water structure and microscopic picture of gas hydrate formation.

8.3.2 Microscopic conceptual picture of gas hydrate formation

To discuss the possible mechanisms of the dual effect of sodium halides on gas hydrate kinetics, we should first briefly describe the pathway of gas hydrate formation. As per the labile clusters hypothesis [6], gas hydrate nucleation originates from the formation of water clusters around dissolved guest molecules in such process known as hydrophobic hydration. The water at hydrophobic hydration shells is proposed to be in “pre-hydrate” structure. This theory has been intensively tested by both experimental measurements (e.g., [10-12]) and computer simulations (e.g., [13-15]) to determine water structure on hydration shells and the coordination number. Most of the outcomes appeared to support the hypothesis since they proved the existence of hydration shells around hydrophobic molecules, in particular, methane molecules. However, both computer simulation and experimental measurements have shown that the number of water molecules in the hydration shell of methane in aqueous solution (so-called coordination number) is around 19 [12, 16] which is smaller than the expected values of 20 and 24 for sI small ($5^{12}$) and large ($5^{12}6^2$) cages, respectively. Hence, the hydration shells have been proposed to undergo transformations, through various intermediate states, before accomplishing the structural conformation of clathrate. I visually simplify this process as depicted on Figure 8.5.
Figure 8.5 Conceptual diagram of the formation of clathrate cages via hydrophobic hydration.

As the transformation progresses, the size and the structural conformation of hydration shells change by establishing and breaking hydrogen bonds, and water clusters undergo through different high-energy states such activation barriers [6]. Consequently, hydrophobic hydration shells can only form and then transform to gas clathrate cavities if the thermodynamic driving force of formation and transformation surpasses activation barriers. This argument explains why gas hydrate can nucleate at a certain region of temperature and pressure. Once clathrate cavities have formed in solution, they develop to construct unit cells by vertex-linking or face-sharing and then further grow into gas hydrate crystals.

8.3.3 Possible effects of halide ions on gas hydrate nucleation

The enclathration of gas in neat water, as described in Section 8.3.2 is thermodynamically unfavourable due to the negative entropy change and partial loss in the number of hydrogen bonds associating with the process of enclathration. Consequently, the formation of first hydrophobic hydration shells of methane in neat water is thermodynamically difficult. Apparently, this thermodynamic barrier is observed as the existence of metastability of gas hydrate system.

In sodium halide solutions, an ion-specific effect causing the extraordinary promotion of gas hydrate kinetics is possibly the hydrophobic nature of halide ions. It has been suggested via both experimental (e.g., [17-19]) and simulation (e.g., [20]) studies that large-size and polarizable halide ions such as iodide display a hydrophobic nature and, therefore, function as hydrophobic entities whereas small-size and charge-dense ions such as fluoride cannot play the same role. Discussion on the physics behind hydrophobic nature of ions is complicated and beyond the scope of this paper. This extraordinary concept, however, is useful for approaching a reasonable explanation of the promoting behaviour of sodium halides.
As an ion, iodide is easily hydrated forming a solvation shell, compared to methane. Also considered as a hydrophobic entity, the hydration of iodide is hydrophobic hydration and its solvation shell, therefore, is a hydrophobic hydration shell. In contrast to the case of multivalent ions or small and charge-dense ions, iodide-water interaction is weaker than water-water interaction [21]. I, therefore, propose that even being too weak to fully collapse local water structure, the weak iodide-water interaction is still sufficiently strong to structurally rearrange adjacent water molecules into a fashion similar to water structure on the hydration shell of methane. Therefore, the existence of these similar hydrophobic hydration shells is proposed to facilitate the occurrence of the hydrophobic hydration of methane. In the other words, the hydrophobic hydration shells of iodide ions play the important role of the seeding for gas enclathration.

Obviously, the hydrophobic nature of halides is the central basis for this hypothesis. The idea that polarizable ions have their hydrophobic behaviours has been suggested via computer simulation [20] and the inference from several spectra interpretations [17-19]. The experimental results shown in Table 8.1 further prove the hydrophobic nature of halides. The contact angle between the saturated salt solution and the salt crystal surface is a measure of the hydrophobicity of the ions. For example, the zero contact angle for NaF shows that fluoride likes water and is strongly hydrated by water, whereas the contact angle of 12.7° for NaI shows that iodide does like water as fluoride but it is not hydrated by water as much as fluoride; indeed, of the halides investigated, iodide is the most hydrophobic halide. The results for the contact angles in Table 8.1 evidently show NaI is the most hydrophobic, followed by NaBr whereas NaCl and NaF are hydrophilic. As these salts share the same sodium cation, the difference in hydrophobicity is logically due to the halide anions. See Section 11.4.1 in Appendix for the measurement of contact angle.

It is evident from these results for contact angle that as fluoride is very hydrophilic [18] it cannot play the function as effectively as iodide does. In contrast, fluoride ion strongly interacts with adjacent water molecules electrostatically and disrupts the local water structure radically, a phenomenon known as the disruption of water structure by ions which is reported in the literature [1, 22]. Consequently, gas hydrate formation is hindered as the initiation of gas hydrate nucleation needs to associate with tetrahedrally ordered water structure.
Table 8.1 Contact angle (CA) between salt crystal surfaces and their saturated solutions

<table>
<thead>
<tr>
<th>Surface</th>
<th>0 s</th>
<th>1/15 s</th>
<th>5/15 s</th>
<th>Equilibrium (after 1 s)</th>
<th>CA (degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaF</td>
<td>![Image of NaF contact angle]</td>
<td>![Image of NaF contact angle]</td>
<td>![Image of NaF contact angle]</td>
<td>![Image of NaF contact angle]</td>
<td>0.0 ± 0.0</td>
</tr>
<tr>
<td>NaCl</td>
<td>![Image of NaCl contact angle]</td>
<td>![Image of NaCl contact angle]</td>
<td>![Image of NaCl contact angle]</td>
<td>![Image of NaCl contact angle]</td>
<td>0.0 ± 0.0</td>
</tr>
<tr>
<td>NaBr</td>
<td>![Image of NaBr contact angle]</td>
<td>![Image of NaBr contact angle]</td>
<td>![Image of NaBr contact angle]</td>
<td>![Image of NaBr contact angle]</td>
<td>6.7 ± 0.2</td>
</tr>
<tr>
<td>NaI</td>
<td>![Image of NaI contact angle]</td>
<td>![Image of NaI contact angle]</td>
<td>![Image of NaI contact angle]</td>
<td>![Image of NaI contact angle]</td>
<td>12.7 ± 1.5</td>
</tr>
</tbody>
</table>

Furthermore, the existence of transition concentrations is possible because at these concentrations, the number of ions and, therefore, their hydration shells is adequate for the seeding for nucleation. If ion density is higher than transition concentration, there occurs the competition between ions and gas molecules to gain water for hydration. As ions bind water more strongly than gas molecules do, gas molecules lose their ability to constrain water to establish hydrophobic hydration shells (which are pre-hydrate cages). Another consequence is also a reduction in gas solubility in concentrated salt solutions. This argument explains the inhibiting effect of salts at high concentrations.

The final point worth discussing is the salt collection by gas hydrates. Gas hydrate is conventionally believed to be salt-free and, therefore, expected to be a novel method for desalination. However, my hypothesis of considering hydration shells of polarizable ions as seeds for gas hydrate nucleation should lead to the consequence that gas hydrate crystals must contain ions, i.e., these ions must be encapsulated in initial seeds of gas hydrate. Indeed, the results of the chemical assaying of the products and mass balance, as shown in Table 8.2, support my hypothesis. Evidently, the synthesized methane hydrate was not salt-free. These results are consistent with
recent results from an experimental study on CO$_2$ hydrate by Farhang et al. [5] and computer simulation by Qi et al [23]. Furthermore, the recovery of NaI with hydrate is also higher than recovery of NaF. A possible reason is that as NaI is more hydrophobic, it involves more actively in the nucleation of gas hydrate, as per my hypothesis. Consequently, a larger number of iodide ions are encapsulated in gas hydrate crystals, as the seeds for gas hydrate nucleation. See Section 11.4.1 in Appendix for the measurement of salt concentrations in Table 8.2.

**Table 8.2** Mass balance showing the salt distribution in methane hydrates

<table>
<thead>
<tr>
<th>Salt</th>
<th>Mass (g)</th>
<th>Sodium concentration (g/g)</th>
<th>Salt recovery* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Feed</td>
<td>Hydrate</td>
<td>Waste</td>
</tr>
<tr>
<td>NaF</td>
<td>80.018</td>
<td>32.540</td>
<td>47.372</td>
</tr>
<tr>
<td></td>
<td>80.087</td>
<td>34.762</td>
<td>45.282</td>
</tr>
<tr>
<td></td>
<td>80.061</td>
<td>37.999</td>
<td>42.024</td>
</tr>
<tr>
<td>NaI</td>
<td>80.188</td>
<td>41.150</td>
<td>38.786</td>
</tr>
<tr>
<td></td>
<td>80.228</td>
<td>40.142</td>
<td>40.015</td>
</tr>
<tr>
<td></td>
<td>80.212</td>
<td>45.440</td>
<td>34.772</td>
</tr>
<tr>
<td></td>
<td>80.227</td>
<td>39.522</td>
<td>40.402</td>
</tr>
</tbody>
</table>

(*mass of salt in the hydrate phase divided by the total mass of salt in the feed

### 8.4 Conclusion

A series of experiments were successfully conducted to investigate the formation of methane hydrate in water and sodium halide solutions. The changes in pressure and temperature during the methane hydrate formation were measured as a function of time and concentration of NaF, NaCl, NaBr and NaI. The gas consumption, growth rate, induction time and maximum gas consumption were determined. The experimental results show the dual effect of the salts on methane hydrate formation. While it has been widely reported that salts are inhibitors to gas hydrate formation, the outcome of this research evidently proves that sodium halides can be either a promoter at low concentration or an inhibitor at high concentration. Furthermore, large and soft (polarizable) ions like iodide were shown to be more effective promoters whereas small and hard (high-charge
density) ions like fluoride were observed to be an effective inhibitor. I propose that the difference in hydrophobicity of halides gives rise to this experimental observation. This hypothesis is supported by the results of the contact angle measurements and the salt recovery by the methane hydrate. This work provides experimental evidence of ion-specific effect on gas hydrate formation.

References


Chapter 9

Hydrophobic Effect on Gas Hydrate Formation in the Presence of Additives

Abstract

Additives like surfactants, polymers, salts, and hydrophobic particles are well known (and used) to influence gas hydrate formation (GHF). This paper reviews and discusses the mechanisms of their effects. Apparently, the effects of additives on GHF vary greatly from one additive to another. Even a given additive can change from a promoter to an inhibitor and vice versa when the working condition is changed. The available literature cannot explain the diverse effects of additives. I argue that hydrophobic effect plays a critical role in gas hydrate formation. A dissolved hydrophobe organizes the surrounding water into a clathrate-like structure and thereby promotes hydrate formation. A hydrophilic, however, disrupts the surrounding water structure and inhibits hydrate formation. Moreover, cooperative hydrophobic interactions create an increased gas concentration around a hydrophobe which also favors the hydrate formation. In contrast, a hydrophilic competes with the gas for water and thereby hinders hydrate formation. Especially, when the additive is an amphiphile, the observed effect is a result of the competition between the hydrophobic moiety (a promoter) and hydrophilic moiety (an inhibitor). This hypothesis provides a universal explanation for the various effects of hydrate additives.

Published in Energy & Fuels 31 (2017), 10311-10323
9.1 Background context

In Chapters 5 – 8, I have established significant evidence for the molecular understanding of gas hydrate formation. The findings fill a number of major knowledge gaps in the current literature and uncover the critical role of the local water structure at the interfaces in gas hydrate formation. Specifically, the findings have shed new insights into the effect of interfacial water alignment, hydrophobic hydration, hydrophobic effect and ion-specific effect on gas hydrate formation. This chapter incorporates all of my current findings and the recent findings in the literature into a general picture. The aim is to establish a universal mechanism that governs the effect of additives on the formation of gas hydrates. In this chapter, I review the general concepts and the effects of additives on gas hydrate formation before developing a hypothesis of hydrophobic effect on gas hydrate formation. As it will be justified in this chapter, this hypothesis can serve as a universal explanation for the promotion and inhibition of gas hydrate formation in the presence of various additives. The hydrophobic effect hypothesis therefore fills the big gap in the current literature which mainly focuses on macroscopic observations and descriptions of the effects of different additives on gas hydrate formation.

Although the literature review has been presented in Chapter 2, the relevant literature is reviewed in this chapter. This literature review is necessary because it establishes a background context for introducing the hypothesis of hydrophobic effect on gas hydrate formation. Furthermore, the reviewed literature in this chapter is discussed deeply and includes my own published results in Chapters 5-8.

9.2 Gas hydrates

Gas hydrates (or gas clathrate hydrates) are ice-like crystalline solids comprising water and suitable gases. The water molecules (the host) form a cage-like hydrogen bonded structure which encapsulates the gas molecules (the guest) inside, and the encaged gas molecules, in turn, exert a multi-directional force to prevent the cage-like structure from collapsing [1, 2]. Such host-guest cooperative interaction makes gas hydrates more thermodynamically stable than ice (i.e. at a given pressure, gas hydrates can form at a temperature well above the freezing point of water).

Despite such astounding simplicity of their chemical composition, gas hydrates have been a topic of enduring interest. Since first discovered in 1810 by Sir Humphrey Davy [1], clathrate hydrates have increasingly attracted a widespread attention of researchers. Even though, over the subsequent century, gas hydrate research was merely for the satisfaction of scientific curiosity. Only from 1934 when Hammerschmidt [3] confirmed that clathrate hydrates cause subsea pipelines
plugging, these inclusion compounds were considered as a nuisance to flow insurances [2, 4, 5]. Indeed, Hammerschmidt’s finding sparked a flourishing growth in hydrate research, with a primary goal being for the prevention of hydrate formation inside transmission lines. From the late of 20th century, many promising applications of gas hydrates started to be conceptualized and demonstrated, including gas storage and transport [6-9], gas separation [10-13] and sequestration of anthropogenic CO₂ [14-19]. Such new perspective on clathrate hydrates has further drawn the attention of academia into this field. Also, the research started to focus on gas hydrate promotion, in parallel with the pre-existing hydrate inhibition direction. Nowadays, gas hydrates have become an applied science with a dynamic growth in the number of scientific publications and form dedicated themes in many scientific journals. Here I view and discuss the molecular mechanisms of the effects of additives on gas hydrate formation. In particular, I discuss the critical role of hydrophobic effect in governing gas hydrate formation. I provide a universal explanation for the diverse effects of additives on gas hydrate formation.

9.3 The formation of gas hydrates

9.3.1 Macroscopic description and molecular concepts

![Figure 9.1](image.png) A typical T-P graph showing different stages involved in gas hydrate formation process. The guest used was methane. The experiment was conducted in an isochoric reactor at initial pressure of 7.5 MPa and target temperature set to 0.5°C [20].

Gas hydrates form spontaneously when water contacts the gas under elevated pressure and low temperature [2, 5]. Figure 9.1 shows a typical T-P graph (T: temperature, P: pressure) recorded from an isochoric hydrate reactor [20]. The sharp rise in T coupled with a huge drop in P indicates the onset of the exothermic formation of gas hydrate inside the reactor. The waiting period between the point of time when T&P fall into the hydrate-forming condition and the onset of hydrate formation is described as the induction time. At the microscopic scale, it is the time needed for the
gas to dissolve into water to produce a supersaturated solution and for the water structure to rearrange itself to accommodate the gas and form initial hydrate crystals.

In nature, gas hydrates form naturally in the locations where the forming condition is met such as in permafrost regions or marine sediments with a water depth of between hundreds and thousands of meters [21]. The temperature and hydrostatic pressure in those locations fall into gas hydrate stability zone which sustains the enclathration of natural gas by marine water. Interestingly, CO$_2$ hydrate formed rapidly when liquid CO$_2$ was disposed directly onto ocean floor at a water depth of 3650 m [22]. This experimental observation supports the idea of sequestration of CO$_2$ in subsea locations [15, 23].

Despite such clear macroscopic observations, the molecular picture of gas hydrate formation remains poorly understood. Especially, the time-dependent (kinetic) properties are the most challenging domain in gas hydrate research [24, 25]. To date, the molecular mechanism of gas enclathration remains controversial [1, 26-28]. Amongst few hypotheses available in the literature [1, 26-28], the labile clusters theory [1, 26] probably provides the most insightful description of the formation mechanism. This theory was developed by Sloan et al. based on a classical “iceberg” model originally proposed by Frank and Evans [1]. It considers gas hydrate nucleation initiates from building locally structured water clusters around individually dissolved gas molecules (known as labile clusters or hydrophobic hydration shells). Under the hydrate-forming condition, the hydration shells transform into gas hydrate cages. Then, the cages agglomerate into hydrate nuclei via face-sharing. When the nucleus size exceeds a critical value, the nuclei grow rapidly into big hydrate masses (Figure 9.2) [1].

![Figure 9.2 Mechanism of gas hydrate formation through labile clusters hypothesis [1].](image_url)

Significant research efforts based on experimental measurements [29-31] and computer simulations [32-34] have sought the evidence of labile clusters. The majority of the outcomes support the existence of a local water structure (hydration shell) around a dissolved guest, in
particular, a methane molecule. Even though, the results indicate that the number of water molecules on a hydration shell of methane (the coordination number) is around 19 [31, 35], which is smaller than the desired values of 20 for small sI (5^{12}) and 24 for large sI (5^{12}6^2) cages. Hence, the hydration shells must undergo a structural transformation, by adopting water molecules from the bulk, through various intermediate states before accomplishing a correct conformation of clathrate hydrate. The time needed for such structural rearrangement and transformation is apparently manifested by the induction period in gas hydrate experiments.

9.3.2 The formation of gas hydrate at the interface

Gas hydrate formation normally initiates at the gas-water interface rather than in the bulk liquid [25]. This characteristic is highly important. It suggests that interface-active agents may affect hydrate formation more effectively than bulk-active ones do. It also infers that the interfacial water needs to be accounted for when explaining gas hydrate phenomena. The interfacial formation of gas hydrates is evidenced by the occurrence of a hydrate thin film at the guest-water interface (in quiescent condition) [36-38]. The film stops growing in its thickness when it becomes diffusion-resistant and thereby hinders the mass transfer across the interface [36]. For example, the final thickness of methane hydrate film was reported to be in between 20-100 μm depending on experimental condition [36]. The formation of hydrate film was more observable in the system containing a small water droplet placed in a guest phase or a small guest bubble placed in an aqueous phase [37-39]. Figure 9.3 shows the occurrence of a methane hydrate film at the surface of a water droplet in methane environment [39].

Figure 9.3 The formation of a methane hydrate thin film at a methane-water interface [39]. The initiation and propagation of a methane hydrate film is clearly observed on the water droplet’s surface

Figure 9.4 explains the mechanism of hydrate formation at a methane-water interface [40]. First, CH₄ molecules transfer across the interface into water. Then the interfacial water forms hydrate cages around dissolved CH₄ molecules right under the interfacial plane. Finally, the cages
agglomerate into a hydrate crystal. The resulting hydrate crystal then obstructs the dissolution of methane into water. Consequently, no further hydrate growth can take place under the interface. Therefore, only a hydrate film is formed. In contrast to the quiescent system, in an agitated system, the turbulence breaks the film and the convection flow conveys the hydrate nuclei into the bulk where they grow into big hydrate masses [1].

![Dissolution Nucleation Growth Water-methane interface](image)

**Figure 9.4** Methane hydrate formation at methane-water interface [40]. Three steps involved are shown on the figure.

### 9.4 The effects of additives on gas hydrate formation

The formation of gas hydrates is very sensitive to the impurity of the medium. The presence of any foreign entities other than water and the guest can cause substantial effects on thermodynamic and kinetic properties of gas hydrate systems. The foreign entities (additives) may be intentionally added to hydrate systems to control the formation kinetics, or they may present in hydrate systems naturally such as dissolved salts, bio-surfactants and colloids. In this section, I review the effects of important additives on gas hydrate formation and discuss the existing explanations for their effects. The reviewed literature in this section is helpful for the general discussion in Section 9.5.

#### 9.4.1 The effects of thermodynamic inhibitors

Thermodynamic hydrate inhibitors (THIs) are the additives that shift the phase equilibrium of a hydrating system to lower temperature and higher pressure, thereby, inhibiting the formation of gas hydrates in a prevailing condition. Systematic investigations into hydrate inhibitors were triggered in 1934 when Hammerschmidt [3] confirmed that clathrate hydrates are responsible for subsea pipeline plugging. The best known THIs are alcoholic compounds (e.g. methanol, ethylene glycol, etc.) and inorganic salts [4, 41, 42]. Since THIs affect the bulk phase of hydrate system, they need high dosages (30-50 mass %) to give a satisfactory inhibition performance [42-44]. Such high dosages lead to serious concerns about the operational and environmental costs [42-44].
Fundamentally, it is widely agreed that THIs inhibit gas hydrate formation by decreasing the activity of water. THIs are highly polar molecules (or ions in the case of salts) which bind water strongly by hydrogen bonds (or by electrostatic forces for ions). The strong binding leads to increased competition with the hydrate former for water. Consequently, there is less water available for forming a hydrate with the gas [1]. The effectiveness of a THI depends upon its capability of binding water [41]. For example, ethanol and ethylene glycol have similar molar volumes, but ethylene glycol has two hydroxyl groups available for hydrogen bonds while ethanol has only one. Consequently, ethylene glycol gives a better hydrate inhibition than ethanol does [41]. Similarly, multivalent ions bind water more strongly than large-size monovalent ions do [45]. As a result, multivalent ions are better THIs compared to large-size monovalent ions.

However, a number of THIs also exhibit as hydrate promoters when they are used at low concentration. For example, experiments have reported a promoted methane hydrate formation in dilute alcoholic solutions [1, 46, 47]. A similar promotion effect was also observed for CH₄ and CO₂ hydrate formation in dilute sodium halide solutions [48-50]. The fundamentals underpinning such promoted hydrate formation in the dilute solutions of THIs cannot be explained by the available literature. In Section 9.5, I present an explanation for this peculiar effect.

9.4.2 The effects of low-dosage hydrate inhibitors on gas hydrate formation

Unlike THIs which affect the bulk phase of hydrate-forming systems, low-dosage hydrate inhibitors (LDHIs) are interface-active agents which influence the interfacial properties of gas hydrates. The use of LDHIs is of increasing interest owing to their low operational dosages, typically less than 1 mass % [43, 44]. LDHIs are conventionally categorized into kinetic hydrate inhibitors (KHI) and anti-agglomerants (AAs) which are different from each other by the acting mechanisms. While KHI act primarily as gas hydrate anti-nucleators, AAs allow gas hydrates to form but prevent hydrate nuclei from further agglomerating into big hydrate masses [43]. The classical KHI are vinylic polymers, of which, polyvinylpyrrolidone (PVP), polyvinylcaprolactam (PVCap) and antifreeze proteins (AFPs) are the most popular [4, 51]. AAs are surface-active compounds such as alkyl aromatic sulfonates or alkylphenyethoxylates [44]. Beside these traditional LDHIs, a vast number of new LDHIs are being introduced. Some of them are listed in Table 9.1.

It is proposed that LDHIs inhibit gas hydrate formation via binding to the surface of an ensuing hydrate nuclei [52]. The adsorption of LDHIs molecules on the surfaces of hydrate nuclei disrupts the growth of hydrate crystals [52]. However, recent studies have shown that an accelerated
hydrate growth can occur in the presence of LDHIs [53-55]. For example, it was found that while 0.5 and 1.5 mass% of PVCap could suppress the nucleation and growth rate of gas hydrate efficiently, 3.0 mass % of this agent induced a catastrophic hydrate growth [54]. In general, the presence of LDHIs can retard the nucleation and growth of gas hydrate within a certain period after which a fast growth takes place steadily [53, 54, 56]. The reason for such catastrophic hydrate growth is not clear [53]. Therefore, further fundamental investigations into this phenomenon are needed.

Table 9.1 New types of LDHIs reported in the recent literature

<table>
<thead>
<tr>
<th>LDHIs</th>
<th>Predominant effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pectin</td>
<td>66% reduction of working dosage and 10-fold increase in effective time in comparison with typical KHI s [57]</td>
</tr>
<tr>
<td>Amino acids</td>
<td>Good inhibition capacity and environmental friendliness [58-60]</td>
</tr>
<tr>
<td>Poly-carbonyl amides</td>
<td>Effective LDHIs [61, 62]. Much better inhibition achieved when combined with nonylphenol ethoxylates or poly ethylene glycol [63]</td>
</tr>
<tr>
<td>Ionic liquids</td>
<td>Good inhibition capacity [64, 65]</td>
</tr>
<tr>
<td>Natural products (NPs)</td>
<td>NPs like chitosan [66] and starches [67] are promising green LDHIs.</td>
</tr>
<tr>
<td>Synergists</td>
<td>The addition of a synergist(such as L-tyrosine [68], poly ethylene oxide [69], NaCl [70], ionic liquids [65] and so on) enhances the inhibition performance of the used LDHIs</td>
</tr>
</tbody>
</table>

9.4.3 Surfactants effects on gas hydrate formation

9.4.3.1 Physicochemical characteristics of surfactants

Surfactants are amphiphilic compounds. Each surfactant molecule consists of a hydrophilic (water-liking) head and a hydrophobic (water-hating) hydrocarbon tail (as shown in Figure 9.5a for sodium dodecyl sulfate). Due to such special molecular structure, surfactants have a tendency of minimizing the exposure of the hydrophobic tails to aqueous phase [71]. As such, surfactants prefer adsorbing on the hydrophobic-aqueous interface with hydrophilic heads remaining in the solution and hydrophobic tails spreading into the hydrophobic phase (Figure 9.5b). Otherwise, when the interfacial adsorption is saturated, they aggregate to form micelles in solutions (Figure 9.5b). The micellization takes place only when the concentration of the surfactant is higher than a certain value.
called critical micellar concentration (CMC), and the solution temperature is above a certain value called Krafft point (Figure 9.5c). Both CMC and Krafft point are specific to each surfactant [72].

**Figure 9.5** The amphiphilic structure of SDS surfactant (a); dodecyl sulfate (DS⁻) adsorption on solution surface and DS⁻ micelle formation in bulk (b); the Krafft point of SDS surfactant (c). On Figure (b), the gas phase and the counter ions (Na⁺) are omitted for clarity.

The presence of surfactants in a solution induces substantial changes in physicochemical properties of the system. Interfacial adsorption of surfactants decreases the interfacial tension between the solution and the adjacent phase [73] which may affect the mass transfer across the interface. It may also carry charges to the interface and subsequently influences the orientation and mobility of interfacial water [20, 74, 75]. The presence of surfactants increases the solubility of gases in aqueous solutions [76-78]. Moreover, due to its amphiphilic nature, a surfactant molecule produces two opposite effects on the local water structure. The hydrophobic tail organizes surrounding water molecules into a clathrate-like cluster, as postulated by Frank and Evans in their well-known work in 1945 [79]. The hydrophilic head (together with the counter ion in the case of ionic surfactant) binds water strongly and disrupts the local water structure, similar to the effect of inorganic salts [80]. These special properties are of great relevance to gas hydrate formation.

### 9.4.3.2 Evidence of surfactants affecting gas hydrate formation

Surfactants probably provide the best acceleration of gas hydrate kinetics. It was reported that sodium dodecyl sulfate (SDS) solution of 284 ppm increased the rate of methane enclathration by 700 times [81]. This surfactant was also investigated intensively in many other works [82-86]. Besides SDS, a huge number of other surfactants were investigated. The most common of them are listed in Table 9.2. In general, it was found that the addition of surfactants could increase hydrate kinetics by the orders of magnitude. Regarding the effect of surfactant types, it was sometimes
noted that anionic surfactants were more effective than non-ionic surfactants yet cationic surfactants were effective only at low concentrations [87]. However, this conclusion might be overgeneralized as dodecyl amine hydrochloride (DAH) and N-dodecylpropane-1,3-diamine hydrochloride (DN2Cl), both are cationic, exhibited a strong promotion of methane hydrate formation at a concentration as high as 3000 ppm [88]. Interestingly, some surfactants display better promotion performances when are mixed. For example, a more efficient promotion was achieved when SDS was mixed with tetrahydrofuran (THF) [82, 84]. Likewise, tetra-butyl ammonium bromide (TBAB) and dodecyl trimethyl ammonium chloride (DTAC) displayed a better promotion under a shared effect than the individual effect of each surfactant [89].

Table 9.2 Common surfactants as gas hydrate promoters

<table>
<thead>
<tr>
<th>Type of surfactants</th>
<th>Name of surfactants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anionic surfactants</td>
<td>Sodium dodecyl sulfate (SDS) [82-86, 90]</td>
</tr>
<tr>
<td></td>
<td>Sodium tetradecyl sulfate (STS) [90]</td>
</tr>
<tr>
<td></td>
<td>Sodium hexadecyl sulfate (SHS) [90]</td>
</tr>
<tr>
<td></td>
<td>Sodium oleate [90]</td>
</tr>
<tr>
<td>Cationic surfactants</td>
<td>Tetra-n-butyl ammonium bromide (TBAB) [11, 13, 89, 91-93]</td>
</tr>
<tr>
<td></td>
<td>Dodecyl trimethyl ammonium chloride (DTAC) [85, 89]</td>
</tr>
<tr>
<td></td>
<td>Dodecyl amine hydrochloride (DAH) [88]</td>
</tr>
<tr>
<td></td>
<td>N-dodecylpropane-1,3-diamine hydrochloride (DN2Cl) [88]</td>
</tr>
<tr>
<td>Non-ionic surfactants</td>
<td>Tetrahydrofuran (THF) [10, 82, 84, 85]</td>
</tr>
<tr>
<td></td>
<td>Ethoxilated nonylphenol [94]</td>
</tr>
<tr>
<td></td>
<td>Tween 80 [95]</td>
</tr>
<tr>
<td></td>
<td>Cyclopentane [96, 97]</td>
</tr>
</tbody>
</table>

9.4.3.3 Governing mechanism of surfactants for gas hydrate formation

The actual mechanism by which surfactants affect gas hydrate formation is poorly understood. There are a number of hypotheses for explaining the accelerated formation of gas
hydrates in surfactant solutions, but they are constructed based on assumptions rather than experimental evidence. For example, it is widely believed that surfactant aggregates (micelles) are responsible for the promoted formation of gas hydrates in surfactant solutions [81]. The micelles are deemed to act as minute gas reservoirs which facilitate the gas dissolution and provide nucleation sites for gas hydrate formation [81]. However, this hypothesis has been under criticism that surfactants, more likely, cannot form micelles in the condition of gas hydrate experiments since the working temperature goes lower than the Krafft point [86, 98]. Even though micelles are still used as a theoretical framework for interpreting the accelerated formation of gas hydrates in surfactant solutions on these days [99].

**Figure 9.6** Illustration of a SDS surfactant micelle in ethane hydrate-forming system [81]. The surfactant micelle is thought to act as a minute gas reservoir thereby facilitates the gas hydrate formation. The grey area in the figure indicates the interior space with high density of ethane.

However, given if micelles do present in hydrate-forming systems, how do they promote hydrate formation still being an open question. The micelles are assumed to act as minute gas reservoirs and provide nucleation sites for gas hydrates [81]. Indeed, a hydrophobic guest (i.e. ethane as on Figure 9.6) can be favorably confined in the interior (core) of the micelle thanks to hydrophobic interactions. Therefore, surfactant micelles may act as minute gas reservoirs in the solution. However, the nucleation of hydrate in the confined space within a micelle may not be possible, due to the exclusion of water. Similarly, the nucleation of gas hydrate on or around a micelle is possibly unfavorable as well, due to the high density of ions in such location (as seen in Figure 9.6). The ions cause a radical disruption of local water structure, similar to in concentrated saline solution [80]. Hence, more convincing evidence is needed to confirm or rule out such role of surfactant micelles in gas hydrate formation. In another hypothesis, it was proposed that the accelerated formation of gas hydrates in surfactant solutions arises from the adsorption of
surfactants on hydrate-liquid interfaces [100]. The observed promotion was attributed to the decrease in interfacial tension due to the surfactant adsorption [86, 100].

**Table 9.3** The effectiveness of surfactants in promoting gas hydrate formation

<table>
<thead>
<tr>
<th>Surfactants</th>
<th>Promotion effectiveness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium dodecyl sulfate (SDS)</td>
<td>Strong [90]</td>
</tr>
<tr>
<td>Sodium tetradecyl sulfate (STS)</td>
<td>Strong [90]</td>
</tr>
<tr>
<td>Sodium hexadecyl sulfate (SHS)</td>
<td>Moderate [90]</td>
</tr>
<tr>
<td>Sodium oleate (SO)</td>
<td>Indiscernible [90]</td>
</tr>
<tr>
<td>Sodium dodecyl sulfate (SDS)</td>
<td>Strong [88]</td>
</tr>
<tr>
<td>Dodecyl trimethyl ammonium chloride (DTAC)</td>
<td>Indiscernible [88]</td>
</tr>
<tr>
<td>Dodecyl amine hydrochloride (DAH)</td>
<td>Strong [88]</td>
</tr>
<tr>
<td>N-dodecylpropane-1,3-diamine hydrochloride (DN2Cl)</td>
<td>Moderate [88]</td>
</tr>
</tbody>
</table>

Nonetheless, the available hypotheses cannot provide a satisfactory explanation for the dual effects (both promotion and inhibition) of surfactants [20, 101]. It is also hard to explain the difference in the effectiveness between surfactants. Table 9.3 shows that the effectiveness of different surfactants is various. For example, Du et al. compared the effects of four surfactants on methane hydrate formation in the same experimental condition [88]. The results showed that sodium dodecyl sulfate has the strongest effect (in terms of decreasing induction time and increasing methane uptake), followed by dodecyl amine hydrochloride and then N-dodecylpropane-1,3-diamine hydrochloride. The fourth surfactant, dodecyl trimethyl ammonium chloride, however, has no discernible effect on methane hydrate kinetics [88]. Similarly, Okutani et al. showed that sodium dodecyl sulfate and sodium tetradecyl sulfate enhance gas hydrate kinetics strongly while the effect of sodium hexadecyl sulfate is lesser [90]. In contrast, sodium oleate has no discernible effect [90]. The available literature is insufficient for explaining these experimental data. In Section 9.5, I discuss the possible explanation for these data.
9.4.4 The effects of hydrophobic particles on gas hydrate formation

9.4.4.1 The hydrophobicity of solid surfaces

The term hydrophobicity describes the water-hating characteristics of material. It is macroscopically measured by the non-wettability of a surface. The opposite is hydrophilicity which indicates the wettability of a surface. Quantitatively, the contact angle of a water droplet on a surface is a measure of surface hydrophobicity (Figure 9.7). In gas hydrate formation, the involvement of solid surfaces is inevitable. There always presents the surface of equipment. Likewise, the formation of natural gas hydrates in geological sediments is always affected by the surfaces of minerals, rocks and solid masses. In many cases, solid particles are intentionally added to hydrate-forming systems as hydrate additives, amongst them hydrophobic fumed silica powder is the best known. This powder is of ultrafine size with the surface being coated by alkyl chains [102]. In gas hydrate experiments, it is mixed with water to a proportion of 1-5 mass % by using a high-speed blender to disperse water phase into minuscule droplets whose surfaces are fully covered by the powder [6, 7, 103]. The resulting mixture is apparently dry, free-flowing and usually referred to as dry water [6, 7].

![Figure 9.7 Contact angle as a measure of hydrophobicity of a solid surface.](image)

9.4.5 Evidence of hydrophobic particles affecting gas hydrate formation

Previous studies showed that hydrophobic particles (or more strictly saying, hydrophobic solid surfaces) could promote the formation of gas hydrates effectively. Especially, dry water produces an excellent promotion for both carbon dioxide [104] and methane [6, 7, 105] hydrates. For example, the methane uptake was increased from 3 (v/v, gas volume in standard condition per hydrate volume) in ordinary water to 175 (v/v) in dry water, under the same experimental condition [6]. The induction time was also shortened to 5-10 minutes in dry water system [6]. In another work, the effect of surface hydrophobicity of sands on hydrate formation was studied [106]. The results showed a decrease in the induction time, from 576 s for untreated (hydrophilic) sands to 71 s for treated (hydrophobic) sands [106]. Furthermore, hydrate formation was more deterministic (less stochastic) when hydrophobic sands were used [106].
Carbon-based materials also attracted the widespread attention of researchers. For example, methane hydrate formation in confined spaces of activated carbon was studied [8]. The results showed an ultrafast hydrate formation with an unprecedented high methane uptake, namely 24 g CH₄ per 100 g dry activated carbon, achieved under mild condition (2°C and 3.5 MPa) [8]. Similarly, graphene oxide particles [107] and multi-walled carbon nanotubes [108] were found to provide a good hydrate promotion. Table 9.4 presents a number of common hydrophobic solid surfaces that were used as hydrate promoters. From these data, it suggests that the hydrate formation is possibly governed by the surface hydrophobicity rather than by the chemical nature of the substrates.

**Table 9.4 Effects of hydrophobic solid surfaces on gas hydrate formation**

<table>
<thead>
<tr>
<th>Solid surfaces</th>
<th>Predominant effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrophobic fumed silica (dry water)</td>
<td>Gas uptake increased from 3 (v/v) in ordinary water to 175 (v/v) in dry water with short induction time [6]. No agitation needed [6, 7]</td>
</tr>
<tr>
<td>Hydrophobized silica sands</td>
<td>Induction time decreased from 576 (s) in original (hydrophilic) sand beds to 71 (s) in treated (hydrophobic) sand bed; Induction time was more reproducible in hydrophobic sand beds [106]</td>
</tr>
<tr>
<td>Hydrophobized glass beads</td>
<td>Shortened induction time and increased hydrate formation rate. No agitation needed [109]</td>
</tr>
<tr>
<td>Metallic surfaces</td>
<td>Shortened induction time and enhanced final water conversion [110]</td>
</tr>
<tr>
<td>Wet nanopore activated carbon</td>
<td>Unprecedented high gas uptake (24 g methane per 100 g dry activated carbon) with ultrafast hydrate formation kinetics [8]</td>
</tr>
<tr>
<td>Carbon nanotubes</td>
<td>The gas uptake increased by 300% with shorter induction time compared with pure water [108]</td>
</tr>
<tr>
<td>Graphene oxide</td>
<td>The induction time decreased by 96% compared to the case of pure water [107]</td>
</tr>
</tbody>
</table>

**9.4.5.1 Governing mechanism of hydrophobic particles for gas hydrate formation**

The promoted hydrate formation in the presence of hydrophobic particles is conventionally attributed to the increased interfacial area [6, 8]. For example, the average size of dry water (water droplets covered by hydrophobic silica powder) was found to be 20 μm [6]. Dry water, therefore, is deemed to provide an adequate gas-water contact for a fast hydrate formation [6]. Similarly, the
ultrafast methane hydrate formation in activated carbons was attributed to the facilitated methane-water contact in the interior pore surface [8]. In other words, hydrophobic particles are assumed to promote gas hydrate formation through a kinetic route.

However, it was also found that dry water shifted the equilibrium of methane hydrate to a higher temperature and a lower pressure [103]. This effect indicated that dry water acted as a thermodynamic promoter rather than a phase-contact facilitator. Moreover, hydrate kinetics was improved by increasing the surface hydrophobicity of the solids [106, 111]. These findings are very interesting, but they cannot be explained by the available literature. In Section 9.5, I present a universal explanation for the effect of hydrophobic particles on gas hydrate formation.

9.5 General discussions

My literature review and discussion in previous sections have indicated a significant deficiency of the current literature for explaining the effects of additives on gas hydrate formation. Previous works were overwhelmed on macroscopic measurements of kinetic and thermodynamic properties of hydrate systems under the presence of hydrate additives [112-114] yet insufficient attention was paid to the fundamental understanding. The macroscopic measurements produce experiment-specific results, the results that depend on the conditions adopted (e.g. type and concentration of additives, type of equipment, etc.) [24]. Consequently, it is difficult to generalize and conceptualize the findings.

In fact, water structure plays a vital role in gas hydrates [1, 115]. Especially, the dynamics of hydrogen bonds is of paramount importance. The labile cluster, the memory effect and the metastability of hydrate systems are all played by hydrogen bonds. However, hydrogen bonds remain to be a long-standing mystery [116-119]. This knowledge gap has created many difficulties in elucidating hydrate phenomena at the microscopic level, which is apparently reflected by slow progress in understanding time-dependent properties of gas hydrates (while the structural properties and thermodynamics have been well documented) [24, 25]. It also leads to difficulties in understanding the effects of additives at the molecular level. The existing explanations for the promoted or inhibited hydrate formation in the presence of additives are additive-specific and experiment-specific, meaning that each of the explanations is only valid for a specific experimental condition. In following sections, I discuss that hydrophobic effect serves as a universal mechanism of the effects of hydrate additives.
9.5.1 Hydrophobic effect in gas hydrate formation

The hydrophobic effect in the context of this paper describes a hydrophobicity-specific effect that an additive introduces to the hydrate system. In other words, it refers to the effect that depends on the hydrophobicity rather than the chemistry of the additive. I argue that the hydrophobic effect plays a key factor governing the effects of additives on gas hydrate formation. I justify this argument as follows.

Figure 9.8 Hypothesis of hydrophobic effect on gas hydrate formation in the presence of a hydrophobic additive

According to a concept postulated by Frank and Evan [79] and confirmed by recent experimental evidence [120], a dissolved hydrophobe organizes the surrounding water into a clathrate-like structure (known as hydrophobic hydration shell). Moreover, the cooperative hydrophobic interaction between the hydrophobe and the gas also create an increased local gas concentration around the hydrophobe [121, 122]. Since the formation of first gas hydrate cages in pure water is thermodynamically difficult (due to a negative change of entropy), the presence of the clathrate-like hydration shells can act as the seeds (nucleation sites) in the solution. The nearby gas molecules then incorporate to the seeds to build up gas hydrate cages. The increased local density of gas around the hydrophobe makes this cooperative nucleation occur faster. This molecular picture is schematically depicted in Figure 9.8. It describes the hypothesis of hydrophobic effect on gas hydrate formation. In fact, the formation of semi-clathrate hydrates of tetra-butyl ammonium bromide (TBAB), tetrahydrofuran (THF) or cyclo-pentane (CP) provides concrete evidence confirming this hypothesis. The solutes (TBA⁺ cation, THF or CP molecule) form their clathrate-like hydration shells first; then the dissolved gas molecules incorporate to the shells to build up gas hydrate structures [93, 123-125].
In the light of this hypothesis, the effect of the hydrophobicity of an additive can be discussed. Purely hydrophobic additives (e.g. CP) produce a greater hydrophobic effect per one dissolved molecule. However, these additives have a poor solubility in water. In contrast, partial hydrophobic additives (e.g. TBA⁺ and THF) produce a lesser hydrophobic effect, but they have good solubility in water. Therefore, it may be difficult to compare the collective effects of additives based on their hydrophobicity. However, it can be guaranteed that for a single dissolved molecule, a better hydrophobicity results in a better hydrate promotion performance. This argument is supported by the experimental observations that tetra-butyl ammonium bromide (TBAB) and tetra-pentyl ammonium bromide (TPeAB) are hydrate promoters, but tetra-propyl ammonium bromide (TPrAB), tetra-ethyl ammonium bromide (TEAB) and tetra-methyl ammonium bromide (TMAB) are hydrate inhibitors [126]. Obviously, TBAB and TPeAB have longer hydrocarbon chains and therefore are more hydrophobic in comparison with TPrAB, TEAB, and TMAB (Figure 9.9).

![Figure 9.9](image.png)

**Figure 9.9** The effects of hydrocarbon chain length (hydrophobicity) of tetra-alkyl ammonium bromide on gas hydrate formation. The single sphere represents the Br⁻ counter ion.

When an additive is hydrophilic, it binds water strongly and disrupts the local water structure. A hydrophile competes with the gas for water. These effects are opposite to the effects of a hydrophobe. Consequently, a hydrophile inhibits gas hydrate formation. Moreover, it is noted that this hypothesis deals with the effects of additives on the nucleation stage of gas hydrate formation. Therefore, it may not be applicable to the additives which affect the growth stage (e.g. anti-agglomerants). In the following sections, I discuss the application of this hypothesis in explaining the effects of various additives on gas hydrate formation.
9.5.2 Hydrophobic effect of amphiphilic compounds on gas hydrate formation

In the light of hydrophobic effect, it is inferred that an amphiphilic molecule creates two oppositely competitive effects on gas hydrate formation. While the hydrophobic part acts as a hydrate promoter, the hydrophilic part (and the counter ion in the case of ionic surfactants) acts as a hydrate inhibitor. The macroscopic observation of promoted or inhibited hydrate formation in the solution of an amphiphilic compound is the reflection of the competition between these two component effects. Therefore, a given additive may have both promotion and inhibition effects as reported experimentally [1, 46, 47, 101, 127, 128], depending on which of the component effects being dominant in the working condition. This molecular picture explains the dual effects (both promotion and inhibition) of many amphiphilic compounds on gas hydrate formation [1, 46, 47, 101, 127, 128].

In a quantitative way, the latest spectroscopic findings have made it possible to quantify the hydrophobic effect on gas hydrate formation. The local water structure around amino acids has been probed and correlated with gas hydrate formation [58, 129, 130]. Amino acids with lower hydrophobicity (having a smaller hydrocarbon group or stronger hydrophilic group) were found to disrupt local water structure strongly and inhibit gas hydrate formation effectively. In contrast, amino acids with higher hydrophobicity enhanced the local water structure and acted as hydrate promoters [58, 131]. These experimental findings provide convincing evidence of the competition between the hydrophobic and hydrophilic moieties of an amphiphilic molecule in affecting gas hydrate formation. The findings thereby support the hydrophobic effect hypothesis.

9.5.3 Hydrophobic effect of solid particles on gas hydrate formation

The analyses of the solution-solid interface by using molecular dynamics simulation and Raman spectroscopy have shown two important findings [111, 132]. First, water structure was enhanced near a hydrophobic surface but disrupted near a hydrophilic surface [111, 132]. These effects respectively share the same physicochemical principle with the effects of a hydrophobe and a hydrophile on local water structure as discussed previously. Moreover, simulation data also showed that gas concentration was increased near a hydrophobic surface while decreased near a hydrophilic surface (Figure 9.10) [132]. Both of the effects (on water structure and gas density) were governed by the hydrophobicity of the solid surface, which agreed with the experimental observations that gas hydrate formation was increasingly promoted by increasing the hydrophobicity of the solid surfaces [106, 111, 132]. These findings indicate that the hydrophobic effect hypothesis is also valid for macroscopic hydrophobe and hydrophile (particles instead of molecules). More importantly, it is inferred that the hydrate formation is governed by surface...
hydrophobicity rather than the chemistry of the solid surface. This is the reason why various solid surfaces with different chemistries can exhibit comparable promotion effects (see Table 9.4).

**Figure 9.10** Simulation snapshots show an increased methane concentration near a hydrophobic surface (a) in contrast with a decreased concentration near a hydrophilic surface (b) [132].

### 9.5.4 Hydrophobic effect of inorganic ions on gas hydrate formation

Inorganic salts are well-known thermodynamic hydrate inhibitors. However, recent experiments have shown a promoted formation of CH$_4$ and CO$_2$ hydrates in dilute NaX solutions (X = I$^-$ and Br$^-$), along with an inhibited formation in the concentrated solutions [48-50]. Here I use the hydrophobic effect hypothesis to explain such a peculiar promotion effect of the NaX. First, it is argued that the peculiar effect of sodium halides on gas hydrate formation arises from the ions-specificity of the halides ions [48]. The ions-specificity states that the effect of ions on water structure is a dependence of their charges and sizes. Large-size and low charge-density monovalent ions (e.g., I$^-$ and Br$^-$) bind water molecules weaker than the water molecules bind themselves [45, 133]. The water molecules around these ions, therefore, form a stronger hydrogen bond network (cage) similar to the hydration of a nonpolar solute [45, 133]. Interestingly, these ions also exhibit a significant surface propensity [134, 135] which property is well known for surfactants. From these special properties, large halides ions (typically I$^-$) are known to bear a hydrophobic nature [134, 135].

Based on the hydrophobic nature of halide ions, the dual effects (both inhibition and promotion) the NaX on gas hydrate formation can be elucidated. At high concentration of NaX, the increased competition between ions and the gas for water results in a shortage of water for gas hydrate formation. Consequently, gas hydrate formation is inhibited. In low concentration regime, however, the competition does not cause a significant effect in the availability of water, yet the presence of cage-like hydrophobic hydration shells of halide ions is proposed to act as seeding for gas hydrate formation (Figure 9.11) [48].
9.5.5 Interfacial water structure under surface adsorption of amphiphilic compounds

The interfacial water structure is of paramount importance given the fact that gas hydrate nucleation takes place at the interfaces [36-40, 136]. Driven by the hydrophobic assembly, hydrophobic or amphiphilic compounds tend to adsorb on the interface for minimizing the exposure of the hydrocarbon moiety to the aqueous solution [121]. The interfaces involved in gas hydrate formation include gas-solution interfaces, hydrate-solution interfaces and solid-solution interfaces (also including equipment wall-solution interface). The interfacial adsorption leads to an increased presence of the additive at the interface. It is, therefore, critical to know the additive-induced changes in the interfacial water first, before being able to elucidate how such changes in the interfacial water affect the subsequent nucleation and growth of the hydrate.

Consider the gas-solution interface for example. Recent experiments have reported an anomalous inhibition of gas hydrate formation in dilute solutions of sodium dodecyl sulfate (SDS) [20, 101]. The results showed that, at a ultralow concentration (e.g., 0.3 mM), SDS had a negligible effect on the bulk solution, but the interfacial adsorption was already significant [20]. As a result, the effect of the SDS in the bulk solution could be neglected. In contrast, the effect of the SDS at the interface was found to be important. At the interface, the hydrophobic tails of the dodecyl sulfate (DS\(^{-}\)) anions were inserted into the gas phase (see simulation snapshot on Figure 9.12a). Therefore, they were deemed to have no considerable effect on the hydrate formation. The effect of the hydrophilic heads at the interface was quantified by using interface-specific techniques (Sum frequency generation vibrational spectroscopy with the aid of MD simulations). The results showed a strong water alignment underneath the surface charge (adsorbed DS\(^{-}\) anions) [20, 137]. Such aligned configuration of water has been proven to be the origin of the anomalous hydrate inhibition in dilute surfactant solutions [20, 137]. Figures 9.12b,c indicate the enclathration of methane in ordinary water (b) and in the aligned water underneath surface charge (c) [20]. The enclathration of
methane is inhibited in aligned water because the driving force of methane enclathration tends to organize the water into a hydrate cage while the interfacial field inclines the water into aligned.

Figure 9.12 The adsorption of DS\textsuperscript{−} anions on the gas-solution interface in ultralow concentration regime (a); the methane enclathration in ordinary water (b) and in the aligned water underneath surface adsorption of surfactants (c) [20]. The negative charges in (c) represent the hydrophilic heads of DS\textsuperscript{−}.

9.6 Conclusion

I have reviewed the effects of important additives on gas hydrate formations. The experimental observations on effects of these additives are extremely diverse. The available literature faces significant deficiencies in explaining the experimental data. I have presented a hypothesis based on hydrophobic effect for understanding gas hydrate formation in the presence of additives. The hypothesis deals with the effects of an additive on the local water structure and local gas concentration, as dependences upon its hydrophobicity. This hypothesis provides a satisfactory reasoning of various effects of hydrate additives. It, therefore, can serve as a universal mechanism of the effects of additives on gas hydrate formation. Even though, future research is needed to quantify this hypothesis and includes the followings.

A quantified correlation between the hydrophobicity of additives, local water structure, and gas hydrate formation would be needed. For “molecular” additives, their hydrophobicity can be changed by altering the hydrocarbon tails and their functional groups. Their effects on local water structure can be quantified by spectral means (e.g., Raman spectroscopy, sum frequency generation vibrational spectroscopy). The effects of hydrophobicity of the additives on clathrate hydrate formation can be determined by kinetics measurements. Indeed, this research direction has recently been undertaken with amino acids [58, 129, 130]. The local water structure around amino acids was probed and correlated with gas hydrate formation [58, 129, 130]. The research outcomes should be expanded to surfactants and other compounds.
Quantifying the hydrophobicity of a solid surface, the water structure in the vicinity of the surface and the kinetics of gas hydrate formation in the presence of the surface would be needed. The hydrophobicity of a solid surface can be changed by surface coating. Water structure in the vicinity of the surface can be quantified by spectral means (e.g., Raman spectroscopy, sum frequency generation vibrational spectroscopy) and computer simulations. The effect of the solid surface (solid particles) on clathrate hydrate formation can be determined by kinetics measurements. From the obtained results, the correlation between surface hydrophobicity, local water structure, and hydrate kinetics can be constructed. This research direction has been successfully performed by different research groups [106, 111, 132]. However, we would need further systematic investigations.

The outcome from these research activities will address gas hydrate promotion and inhibition through the changes in local water structure. Hence, it can provide the molecular and universal understanding of gas hydrate promotion and inhibition. It therefore further validates the proposed mechanism.

References


Chapter 10

Conclusion and Remarks

In this thesis, the kinetics of gas hydrate formation in the presence of surfactants, hydrophobic solid surfaces and sodium halides has been investigated at molecular scales by using synergic combination of experimental, spectroscopic and computational techniques. I have established significant evidence of the critical role of water structure at the interface, the hydrophobic effect and the ions-specific effect on gas hydrate formation (GHF). These findings are new and have scientific and practical significance. Specifically, the key conclusions are as follows.

A surfactant can display an inhibiting or promoting effect on GHF depending on the concentration being low or high, respectively. Interfacial water structure plays a key role in governing GHF. Specially, the water alignment underneath surface adsorption of surfactants gives rise to the inhibition of GHF in dilute surfactants solutions. The perturbation of water structure in the bulk by bulk-residing surfactants is responsible for the promotion of GHF in concentrated surfactant solutions. These findings validate the Hypotheses 1 and 2 and answer Research Questions 1 and 2 in Chapter 3.

The governing role of interfacial water structure is also displayed in the system containing hydrophobic surfaces (including dry water). The hydrophobic effect introduces a structured water network and an interfacial gas enrichment at the hydrophobic solid-water interface in contrast with a disrupted water network and an interfacial gas depletion at hydrophilic solid-water interface. The presence of the structured water network and the interfacial gas enrichment at hydrophobic solid surfaces gives rise to the promotion of GHF by hydrophobic solid particles (including dry water). These findings validate Hypothesis 3 and answer Research Question 3 in Chapter 3.

I showed that sodium halides can act as hydrate promoters when they are used at low concentrations (50 – 70 mM) beside their well-known inhibition effect in high concentration regime. The anomalous promotion effect of sodium halides originates from the hydrophobic nature of large-size and low-charge-density halide ions (e.g., I⁻ and Br⁻). These findings validate Hypothesis 4 and answer Research Question 4 in Chapter 3.

Finally, a hypothesis of hydrophobic effect on GHF is proposed. An additive is a promoter if it is a hydrophobe which organises the surrounding water into a clathrate-like structure and cooperatively interacts with dissolved gases to create an increased gas concentration around it. In
contrast, an additive is an inhibitor if it is a hydrophile which disrupts the surrounding water structure and competes with the gas for water. Especially, when the additive is an amphiphile, the observed effect is a result of the competition between the hydrophobic moiety (a promoter) and hydrophilic moiety (an inhibitor). This hypothesis provides a universal explanation for the various effects of diverse additives on GHF. This theory validates Hypothesis 5 and answer Research Question 5 in Chapter 3.

All in all, this thesis sheds new molecular insights into GHF in the presence of additives and provides steps towards mastering hydrate-based processes in many industrial and environmental applications.
Appendix

11.1 Supporting information for Chapter 5

11.1.1 Surface adsorption of TBA\(^+\) cation evidenced from SFG spectra

The presence of TBA\(^+\) cations on solution surface (as a result of surface adsorption) is evidenced by the occurrence of vibrational modes of alkyl group on SFG spectra (see Figure 11.1). In spectral region between 2800 and 3000 cm\(^{-1}\), the vibrational regime of TBA\(^+\) cation is featured by three predominant peaks centering at around 2880, 2940 and 2975 cm\(^{-1}\) which are assigned to symmetric stretch (SS), stretch-bend Fermi resonance (FR) and asymmetric stretch (AS) of methyl (CH\(_3\)) group, respectively [1, 2]. In addition to methyl (CH\(_3\)) modes, it is straightforward to observe some less predominant peaks among methylene (CH\(_2\)) stretch. However, I am not going to describe comprehensively the spectra of this region since my current interest is on watery hydrogen bond network. The aim here is just to use the spectral information about methyl modes to prove the surface adsorption of TBA\(^+\).

![SFG spectra of alkyl group. The occurrence of vibrational modes of alkyl group on SFG data evidently indicates the presence of TBA\(^+\) on the surface of solution.](image)

**Figure 11.1** SFG spectra of alkyl group. The occurrence of vibrational modes of alkyl group on SFG data evidently indicates the presence of TBA\(^+\) on the surface of solution.

11.1.2 Correlation between TBAB concentration and area of CH bend

On the measured ATR-FTIR spectra, the area of CH bend with three sharp peaks at 2880, 2940 and 2975 cm\(^{-1}\) was calculated as a function of TBAB concentration. Figure 11.2 shows the obtained results, confirming the expected linearity of the ATR-FTIR signal and TBAB concentration. This feature of ATR-FTIR spectra confirms that ATR-FTIR method is bulk-specific.
11.1.3 Calculation of local concentration and surface excess in MD simulation

The MD simulation produces molecular trajectory (or time-dependent coordinates) of the tested system, showing the dynamic movements of all molecular species in the simulation box. To study the surface adsorption of tetra-butylammonium cation (TBA⁺), the simulation box was divided into different slabs in parallel with xy plane, each slab had an equal thickness of 0.5 Å ($\Delta z = 0.5 \text{ Å}$). The local density of TBA⁺ cation and water can be calculated by averaging the number of these species in each slab over the molecular trajectory. The results from this calculation were then used to establish the density profile which shows the local concentration of TBA⁺ and water with respect to the distance from the calculation point to the interface. One of the obtained density profile is shown on Figure 11.3 for the instance of System B in my simulation (which is discussed in Chapter 5).

In Figure 11.3, the local densities of TBA⁺ and water are plotted against the distance from the point of calculation to the Gibbs dividing surface (GDS). In interfacial science, Gibbs dividing surface is a defined plane separating the solution phase and the gas phase and its position is at where local density of water becomes half of the bulk [3]. The negative distance in the horizontal axis indicates that the point of calculation is in the gas phase, and the positive distance directs to the solution phase. It is noted that the density of water (blue curve) in Figure 11.3 is scaled by a factor of 1/25 to match the scale of the graph.
The interfacial concentration (or surface excess) of individual compound can be calculated by numerically integrating the density profile across the interface \([3, 4]\). In particular, the surface excess of TBA\(^+\) was calculated using the following integral.

\[
\Gamma_{TBA} = \int_{-\infty}^{z_0} C_{TBA}(z)\,dz + \int_{z_0}^{\infty} (C_{TBA}(z) - C_{TBA, bulk})\,dz
\]

(11.1)

Where \(z_0 = 0\) is the GDS, and is chosen so that \(\Gamma_{water} = 0\) (ref. \([3]\)). The \(C_{TBA}(z)\) is the concentration of TBA\(^+\) at the distance \(z\) from the GDS, and \(C_{TBA, bulk}\) denotes the concentration of TBA\(^+\) cation in the bulk. Both \(C_{TBA}(z)\) and \(C_{TBA, bulk}\) were read from the density profile.

11.2 Supporting information for Chapter 6

11.2.1 Modulus fitting of SFG spectra

The experimentally measured signals were fitted with theoretical modulus model, using following equation.

\[
I_{SFG} = \text{const} \left| A_{NR} + \sum_{\nu} \frac{A_{\nu}}{\omega_{\nu} - \omega_{IR} - i\Gamma_{\nu}} \right|^2
\]

\[
= \text{const} \left[ A_{NR} + \sum_{\nu} A_{\nu} \frac{\omega_{\nu} - \omega}{(\omega_{\nu} - \omega_{IR})^2 + (\Gamma_{\nu})^2} \right]^2 + \text{const} \left[ \sum_{\nu} A_{\nu} \frac{1}{(\omega_{\nu} - \omega_{IR})^2 + (\Gamma_{\nu})^2} \right]^2
\]

(11.2)

Where \(I_{SFG}\) is the modelled intensity, \(A_{NR}\) is the non-resonant part of the signal, \(A_{\nu}\) is the intensity of the \(\nu^{th}\) mode, \(\omega_{\nu}\) is the frequency of the resonant vibration, \(\omega_{IR}\) and \(\Gamma_{\nu}\) are respectively the IR frequency and damping constant. A detailed description of SFG theory is presented elsewhere [5, 6].
The fitting was performed using least squares algorithm. The resulting $\omega_v$ and $A_v$ define the center position and intensity of the component peak corresponding to the $\nu_{th}$ mode. Figure 11.4 shows an example the fitting outcome.

![Figure 11.4](image)

**Figure 11.4** The fitting of experimental SFG signals using modulus SFG model.

### 11.2.2 The effect of mixing solution on SFG spectra

Figure 11.5 shows the change in SFG spectra when TBAB is added to 0.3 mM SDS solution. The spectrum of the solution of 0.3 mM SDS is shown in blue, and that of the mixed solution of 0.3 mM SDS and 3.6 mM TBAB is shown in green. The observed reduction of SFG intensity in the mixed solution indicates a decrease in water alignment at the interface when TBAB is added. The details of this phenomenon are discussed in Chapter 6.

![Figure 11.5](image)

**Figure 11.5** The effect of the addition of TBAB on the SFG spectra of SDS solution. The concentrations are shown on the graph.
11.3 Supporting information for Chapter 7

11.3.1 The movement of gas molecules to the interfaces

In my simulations, the gas molecules were initially inserted randomly into water phase. During simulations, gas molecules were driven to the hydrophobic surface under the driving force of hydrophobic assembly which results in an increase in gas concentration in the interfacial layer within 10 Å from the hydrophobic solid surface (as presented on Figure 11.6). The data indicates that CH$_4$ moved to the interface at a faster rate than CO$_2$ does. Moreover, the average equilibrium concentration of CH$_4$ in the interfacial region is also higher than that of CO$_2$. These observations are understandable given the point that CH$_4$ is a more hydrophobic gas compared to CO$_2$.

![Figure 11.6](image.png)

**Figure 11.6** The time-dependent gas concentration in the interfacial region within 10 Å from hydrophobic solid surface. The increase in the concentration indicates the movement of gas molecules from the bulk to the interface.

11.3.2 The effect of initial concentration of gas on the density of gas at the interface

Figure 11.7 shows density profiles versus the initial concentration of gas in the aqueous phase in contact with a hydrophobic surface. The initial concentrations of CH$_4$ and CO$_2$ are shown on the legends of the corresponding figures, either in the form of the number of gas molecules inserted in simulation box or their converted molar concentrations. Particularly, the inset on each figure shows the zoom-in scale of gas profile in the bulk region. Generally, it is seen that interfacial gas enrichment (IGE) occurs in every initial concentration of gas. However, the degree of IGE depends strongly upon the initial concentration. This observation is understandable if we consider a fact that the gas molecules in the interfacial region are in the dynamic equilibrium with those in the bulk, which can be expressed by the following expression:
\[ [\text{Gas}]_{\text{interface}} = [\text{Gas}]_{\text{bulk}} \]

where the term on the left hand side represents the interfacial concentration, and the term on the right hand side represents the bulk concentration of gas. In the expression, the forward evolution is favored by entropy change, and the reverse is induced by the hydrophobic assembly driving force. According to the principle of dynamic equilibrium, when the bulk concentration is decreased, the interfacial gas can desorb from the interface to go to the bulk, and vice versa. This principle governs the correlation between the density of the gas at the interfacial region and in the bulk, as numerically exemplified in Figure 11.7.

Figure 11.7 Density profile versus initial concentration of gas at hydrophobic solid-water interface for (a) CH4 and (b) CO2 systems. The results show that interfacial gas enrichment (IGE) depends strongly on the initial concentration of gas as the existence of IGE is governed by dynamic equilibrium.

11.3.3 Instantaneous interface and density of water

Since I was interested to investigate how the water molecules near the solid-water interface are influenced by the surface, it is necessary to define the water molecules based on their distance from the interface. Usually the conventional interface is defined at the position where water density becomes half of the bulk. However, at molecular scale, a mean (unchanged) interface over the complete simulation period might be confusing, rather an instantaneous interface should be used [7]. An instantaneous interface considers the dynamic properties of water at the interface. Here I have calculated the instantaneous interface as defined by Willard and Chandler [7]. I then calculated the water density as a function of the distance in the z direction of water molecules from the interface. Figure 11.8 shows the water density as a function of the distance from the instantaneous interface for the hydrophobic and hydrophilic solid-water surfaces used in my simulations. As shown in the figure, for the hydrophobic solid-water interface, the density
oscillation has two clear maxima. This is consistent with what was observed for the air-water interface in previously reported simulations [7]. I have considered the distance of the first maximum as the first layer and the distance of second maximum as the second layer of interfacial waters. In contrast to hydrophobic solid-water surface, the hydrophilic solid-water interface has only one interfacial region as depicted by one maximum.

![Graph showing density profile of water](image)

Figure 11.8 Density profile of water as a function of the distance from the instantaneous interface.

11.4 Supporting information for Chapter 8

11.4.1 Determination of salt concentration and hydrophobicity

The hydrophobicity of halide salts was determined by measuring the contact angle between a droplet of the saturated salt solution placed on its crystal surface. The saturated solutions were used instead of pure water to avoid the dissolution of crystal surfaces. The large salt crystals were prepared by crystallization from their saturated solution under controlled humidity and temperature. The volume of each droplet was 1 μL. The contact angle was measured using a camera to capture the images of the droplet on the crystal surface. The images were then digitized and processed to calculate the contact angle using a Matlab code developed. The images were taken at the frequency of 15 frames per second.

The concentrations of sodium halides in the feed solutions, gas hydrates (product) and residual solutions (waste) were determined by inductively coupled plasma (ICP) technique.

11.5 List of chemicals used or mentioned in this thesis

Followings are the important chemicals which were used or mentioned in this thesis.
<table>
<thead>
<tr>
<th><strong>Name and structure</strong></th>
<th><strong>Description</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Noted that the molecules are not to scale</td>
<td></td>
</tr>
</tbody>
</table>
| **Tetra-n-butylammonium bromide (TBAB)**   | Formula: C_{16}H_{36}NBr  
MW: 322,368 g/mol  
Dissociate into tetrabutylammonium (C_{16}H_{36}N^+) cation and Br^- anion in an aqueous solution |
| ![TBAB structure](image)                   |                                                                                                                                                 |
| **Sodium dodecyl sulfate (SDS)**           | Formula: CH_{3}(CH_{2})_{11}SO_{4}Na  
MW: 288,372 g/mol  
Dissociate into dodecyl sulfate (CH_{3}(CH_{2})_{11}SO_{4}^-) anion (a surfactant) and Na^+ cation in an aqueous solution |
| ![SDS structure](image)                    |                                                                                                                                                 |
| **Sodium tetradecyl sulfate**              | Formula: C_{14}H_{29}SO_{4}Na  
MW: 316,432 g/mol  
Dissociate into tetradecyl sulfate anion (a surfactant) and sodium cation in aqueous solution |
| ![Sodium tetradecyl sulfate structure](image) |                                                                                                                                                 |
| **N-dodecylpropane-1,3 diamine hydrochloride** | Formula: C_{15}H_{35}N_{2}Cl  
MW: 278,904 g/mol  
Dissociate into C_{15}H_{35}N_{2}^+ (a surfactant) cation and Cl^- anion in aqueous solution |
| ![N-dodecylpropane-1,3 diamine hydrochloride structure](image) |                                                                                                                                                 |
| **Dodecyl trimethyl ammonium chloride**    | Formula: C_{15}H_{34}NCl  
MW: 263,890 g/mol  
Dissociate into C_{15}H_{34}N^+ (a surfactant) and Cl^- anion in aqueous solution |
| ![Dodecyl trimethyl ammonium chloride structure](image) |                                                                                                                                                 |
| **Dodecyl amine hydrochloride**            | Formula: C_{12}H_{28}NCl  
MW: 221,813 g/mol  
Dissociate into C_{12}H_{28}N^+ cation (a surfactant) and Cl^- anion in aqueous solution |
| ![Dodecyl amine hydrochloride structure](image) |                                                                                                                                                 |
| **Sodium oleate**                          | Formula: C_{18}H_{33}O_{2}Na  
MW: 304,450 g/mol  
Dissociate into C_{18}H_{33}O_{2}^- anion (a surfactant) and Na^+ cation in aqueous solution |
<p>| <img src="image" alt="Sodium oleate structure" />          |                                                                                                                                                 |</p>
<table>
<thead>
<tr>
<th>Substance</th>
<th>Formula</th>
<th>MW (g/mol)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tween 80</td>
<td>C₁₀₄H₂₄₂O₂₆</td>
<td>1310</td>
<td>A non-ionic surfactant, good solubility in water</td>
</tr>
<tr>
<td>Cyclopentane</td>
<td>C₅H₁₀</td>
<td>70,1</td>
<td>A hydrocarbon, solubility in water at 25 °C is 156 mg/L</td>
</tr>
<tr>
<td>Tetrohydrofuran (TFH)</td>
<td>C₄H₈O</td>
<td>72,11</td>
<td>A weak non-ionic surfactant, infinite solubility in water (a miscible solute)</td>
</tr>
</tbody>
</table>

References


