RICE UNIVERSITY

Formation and Dissociation Mechanisms of Clathrate Hydrates

by

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ABSTRACT

Formation and Dissociation Mechanisms of Clathrate Hydrates

By

Shuqiang Gao

To better understand hydrate formation and dissociation mechanisms, Nuclear Magnetic Resonance (NMR), Magnetic Resonance Imaging (MRI), and viscosity measurements were employed to examine the hydrate transition processes of tetrahydrofuran (THF) – water (D₂O or H₂O) solution. Specifically, Spin-Lattice Relaxation Time (T₁) and Spin-Spin Relaxation Time (T₂) of THF in D₂O were measured before hydrate formation, during hydrate formation, during hydrate dissociation, and after hydrate dissociation to probe the local molecular ordering changes around THF molecules. Hydrate formation and dissociation patterns were imaged using MRI. The viscosity of THF/H₂O solution was monitored before hydrate formation and after hydrate dissociation using Champion Technologies Hydrate Rocking Cell (CTHRC) to investigate the residual viscosity phenomenon.

NMR relaxation time results demonstrated that the presence of hydrate phase strongly influences the fluid structure of the coexisting liquid phase. T₂ distribution technique was proven to be an effective tool in measuring the dynamic behavior of THF molecules in the hydrate phase and the liquid phase independently and concurrently. Comparison of T₁’s of THF in D₂O solution during hydrate formation with that during dissociation revealed evidence of residual hydrate structures.
remaining in the liquid phase. Residual viscosity (as measured by CTHRC) was absent after THF hydrate dissociation. It was suggested that the residual viscosity observed by other groups after natural gas hydrate dissociation was more likely due to higher than equilibrium gas concentration than residual hydrate clathrate structures.

To enable direct and accurate measurements of gas hydrate behavior in black oil, liquid-state proton NMR spectroscopy was innovatively applied to monitor the water peak area change in the NMR spectrum of water-in-oil emulsion during hydrate formation and dissociation. Because water in the hydrate phase does not contribute to the water peak area in such a spectrum, as water is being converted into hydrate, the water peak area would decrease. Results validated that it is feasible to directly and accurately monitor hydrate behavior in black oil using this technique.
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Chapter 1. Introduction

Gas hydrates,\textsuperscript{[1]} also known as clathrate hydrates, are non-stoichiometric crystalline ice-like compounds composed of cooperative hydrogen-bonded water molecules forming nano-scale clathrate cage structures, which trap smaller guest molecules in nearly spherical cavities. The importance of gas hydrates has been realized in many areas, such as flow assurance during gas/oil productions,\textsuperscript{[2]} potential energy resource,\textsuperscript{[3]} storage and transportation media for some substances,\textsuperscript{[4]} global climate,\textsuperscript{[5]} etc. Discovered in 1810, dedicated research efforts have well established the thermodynamic and structural properties of gas hydrates.\textsuperscript{[1]} However, the question of how gas hydrates form and dissociate on a molecular scale still haunts the minds of many hydrate researchers.\textsuperscript{[6]} This fundamental understanding of the hydrate mechanisms not only serves the natural curiosity of mankind but also contributes to the improvements of practical hydrate applications, such as designing better hydrate inhibitors or promoters.\textsuperscript{[7]}

During deep-water hydrocarbon production, the risk of hydrate plug formation in pipelines demands constant attention and large operational expenditures for treatment.\textsuperscript{[8]} Accurate hydrate phase diagrams and kinetic/transport data are indispensable in assessing hydrate risks in order to adopt appropriate hydrate management strategies and minimize expenses. Unfortunately, hydrate behavior in black oil is poorly understood because direct visual observations are not possible and all current measurements rely on indirect responses such as pressure changes.\textsuperscript{[9]}
Because of the lack of hydrate knowledge in the areas mentioned above, in this work, Nuclear Magnetic Resonance (NMR) and Magnetic Resonance Imaging (MRI), powerful noninvasive tools for obtaining molecular level information,\[^{10, 11}\] were employed to examine the formation and dissociation processes of tetrahydrofuran (THF)/deuterium oxide (D\textsubscript{2}O) hydrate. NMR spectroscopy\[^{12}\] was also applied to directly and accurately measure hydrate behavior in black oil.

The content of this dissertation is organized as follows.

Chapter 2 introduces the basic information about gas hydrates and their implications.

Chapter 3 proposes the key challenges in hydrate applications based on their implications outlined in Chapter 2.

Chapter 4 reviews previous research on the key challenges and identifies what information is lacking.

Chapter 5 summarizes the proposed research, aiming to address the information gaps presented in Chapter 4.

Chapter 6 presents the NMR and viscosity investigation of clathrate hydrate formation and dissociation.

Chapter 7 details the NMR/MRI study of clathrate hydrate mechanisms.

Chapter 8 illustrates the novel application of low field NMR spin-spin relaxation time (T\textsubscript{2}) distribution to clathrate hydrates.

Chapter 9 explains the new technique that uses NMR spectroscopy to characterize hydrate behavior in black oil.

Chapter 10 summarizes the original contributions made in this work.
Chapter 11 offers potential directions for future works.

Appendix A includes an explanation of fundamental knowledge on NMR/MRI in order to aid readers to better understand this work.

Appendix B illustrates the detailed procedures for obtaining experimental data using NMR/MRI apparatus.
Chapter 2. Gas Hydrates

The first discovery of clathrate hydrates is credited to Sir Humphrey Davy,[13] who created chloride hydrate in 1810 when he was experimenting with a chloride-water mixture. Because no practical application of gas hydrates was found in that period, his discovery was treated only as a laboratory curiosity. In 1934, the discovery[14] that it was gas hydrates, not ice, that plugged natural gas pipelines brought a renewed burst of research interests on gas hydrates, especially focusing on determining thermodynamic and structural properties and preventing hydrate plugs. Naturally occurring natural gas hydrates were predicted and found by Russian researchers in the 1960s.[15] This brought another surge of research interests that consider gas hydrates as a potential energy resource and as an important factor affecting global climate changes. The cumulative efforts, beginning with Humphrey Davy, provide tremendous amounts of knowledge about the thermodynamic, physical, and structural properties of gas hydrates and a rich collection of hydrate formers.[1] The rest of this chapter gives a review of hydrate structures, hydrate properties, and hydrate implications.

2.1 Hydrate Structures

Depending on the sizes of the guest molecules included in the gas hydrates, three hydrate structures are traditionally found, which are structure I, II, and H[1] (Table 2.1, Figures 2.1[16] and 2.2). The basic repeating unit in structure I is a primitive cubic lattice consisting of two pentagonal dodecahedra (512) (5 is the number of edges in a face and 12 is total number of this type of face in a cage) and six tetradecahedra (51262) clathrate cages with a total number of 48 water molecules
and a dimension of 1.2 nm. The average cavity radius of each type of cage is 3.95Å and 4.33Å respectively. Methane, ethane, CO$_2$ and Xe are typical structure I hydrate formers. While methane and Xe occupy both small (5$^{12}$) and large (5$^{12}$$^2$) cages, CO$_2$ and ethane are only small enough to dwell in large cages.

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<th>I</th>
<th>II</th>
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<tr>
<td></td>
<td>Small</td>
<td>large</td>
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<tr>
<td>Cages</td>
<td>5$^{12}$</td>
<td>5$^{12}$$^2$</td>
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<tr>
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<tr>
<td>No.of waters / unit cell</td>
<td>48</td>
<td>136</td>
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**Table 2.1** Characteristics of hydrate cages of different structures
(Adapted from Sloan$^{[1]}$)

The repeating unit of structure II hydrate also contains two types of cavities, 16 pentagonal dodecahedra 5$^{12}$ (3.91Å) and 8 hexadecahedra 5$^{12}$6$^4$ (4.37Å) composed of 136 water molecules. It's lattice type is face-centered cubic and its unit dimension is 1.7 nm. Tetrahydrofuran (THF), propane and iso-butane occupy only large cavities in structure II hydrate. O$_2$ and N$_2$$^{[17]}$ are also structure II hydrate formers, and they can fit into both small and large cages. In structure H, a layer of 5$^{12}$ (3.91Å) cavities connects a layer of 5$^{12}$6$^8$ (4.06Å) and 4$^3$5$^6$$^3$ (5.71Å) cavities. In its hexagonal unit cell (a = 1.21nm, c = 1.01nm), 34 water molecules form three 5$^{12}$,
Figure 2.1 Hydrate structures.
Figure 2.2 Comparison of guest molecule sizes and cavities occupied as simple hydrates.\textsuperscript{[1]}
two $5^{12}6^8$, and one $4^35^66^3$. One unique feature of structure H is that both small and large sizes of molecules are required to stabilize the structure. For example, neohexane and cycloheptane, which cannot form hydrates alone, form structure H hydrates with the help of methane. These three hydrate structures are important for the oil/gas industry because the types of hydrocarbons encountered in the field can form all these three types of hydrates.

With the advancement of experimental technologies and continuous research efforts on clathrate hydrates, some new types of hydrate structures at high pressures have been recently identified. Kurossov et al.\textsuperscript{[18]} discovered that under a pressure of 0.8 Gpa [D$_8$] THF and deuterium oxide (D$_2$O) forms an orthorhombic structure with the space group $Pnma$ which has unit-cell dimensions of $a = 12.54$, $b = 11.44$, $c = 6.60$ Å. In this new structure, water molecules form 14-hedra cages with four tetra-, four penta-, and six hexagonal faces ($4^45^46^6$) that are able to pack three-dimensionally without the need for other types of polyhedrons. The stoichiometric composition of a unit cell can be presented as $4T_3\cdot 24D_2O$, where $T_3$ is a $4^45^46^6$ cage. Projection of the structure along the $b$ axis is presented in Figure 2.3.\textsuperscript{[18]}

While investigating dimethyl ether (DME) hydrate using X-ray diffraction, Udachin et al.\textsuperscript{[19]} identified another new hydrate structure that is dense and highly complex (Figure 2.4\textsuperscript{[19]}). It does not have $5^{12}$ polyhedra and can contain $5^{12}6^3$ (P), $5^{12}6^2$ (T), $4^15^{10}6^3$ ($T'$), and $4^25^86^1$ (U) cages (Figure 2.5\textsuperscript{[19]}). This hydrate structure is trigonal, space group P321, $a = 34.995$, $c = 12.368$ Å, and its stoichiometry can be described as $12P\cdot 12T\cdot 24T'\cdot 12U\cdot 348H_2O$. The DME molecules are accommodated
in all three types of large cages (P, T, T), giving an overall composition of DME$\cdot$7.25H$_2$O.

![Diagram of space-filling polyhedron]

**Figure 2.3** Packing and schematic view of the new space-filling polyhedron.

### 2.2 Hydrate Properties and Implications

While the size and composition of hydrate formers determine the type of hydrate structure they form, the hydrate structure influences the hydrate properties. The hydrate properties subsequently dictate the consequences in various situations. The gas hydrate properties that make it practically important are the following. (a) It contains large amounts of gases in a small volume. If all the cages are fully occupied,
one volume of gas hydrate can contain up to 180 volumes (STP) of gas\textsuperscript{[1]} The gas concentration in clathrate hydrate is comparable to that of highly compressed gas, for example, methane gas at 298K and 21Mpa. (b) Gas hydrate's mechanical properties are similar to ice. Its density is higher than typical hydrocarbons. (c) Gas hydrates can form at temperatures far above zero (Figure 2.6) depending on the system pressure, the type of hydrate formers, and its composition, conditions which can be found in natural environments. Most light hydrocarbons require high pressures to form clathrate hydrates. For example, at 10 °C, methane hydrate's equilibrium pressure is about 1000 psia. However, there are some hydrate formers that can form hydrate under ambient pressure, such as THF and ethylene oxide\textsuperscript{[20]} The dissociation temperatures of tetrahydrofuran-H\textsubscript{2}O and ethylene oxide-H\textsubscript{2}O hydrates at their stoichiometric concentrations are ~4.5 °C and ~11 °C.

\[ \text{Figure 2.4 General view of the structure T hydrate as determined by single crystal X-ray diffraction.} \]
Figure 2.5 View of the cages in the structure T hydrate.

Figure 2.6 Hydrate phase diagrams of several common hydrate formers.

Because of the above properties, gas hydrates are of significant importance in the following both beneficial and detrimental ways:

2.2.1 Potential Energy Resource

Because certain natural environments involve low temperatures and high pressures and therefore satisfy the hydrate stability conditions (Figure 2.7), naturally occurring gas hydrates, mainly methane hydrate, have been found in the sediments of the permafrost regions and in the offshore sediments along the continental
margins of many countries\textsuperscript{[21]} (Figure 2.8), including certain areas in the United States, such as Blake Ridge,\textsuperscript{[22]} North Slope Alaska, Cascadia Continental Margin, and off the coast of North and South Carolina. Because of hydrate's capacity to contain large quantities of light hydrocarbons in small volumes, the amount of carbon trapped in these gas hydrate reservoirs has been conservatively estimated to be twice that of all the other types of fossil fuels combined, including petroleum, coal, and conventional natural gas.\textsuperscript{[23]} Consequently, they represent a potentially tremendous source of clean energy, provided that the hydrated gases can be recovered economically through advancements in technology and improvements in the understanding of gas hydrates.

\textbf{Figure 2.7} Illustration of methane hydrate stability region in ocean sediments.
Figure 2.8 Map of known in situ hydrate locations. [1]
Several pilot gas production studies from gas hydrates were conducted in the permafrost regions because they are more accessible than the deep ocean gas hydrate reservoirs. Messoyakha gas hydrate field,[24] located in the north-east of western Siberia, was producing gas from gas hydrates for over 17 years through depressurization and inhibitor injection. Its success is mainly attributed to the fact that it is adjacent to a free gas reservoir. Gas production from the conventional reservoir decreased the pressure. This caused the neighboring gas hydrates to dissociate and the dissociated gas replenished the free gas reservoir. [1] Mallik[25]hydrate research wells, drilled in Mackenzie Delta in far northwest Canada by a joint international effort of six countries led by Canada and Japan,[3] successfully produced a small amount of gas from a very rich gas hydrate deposit by depressurization and continuous heating methods. This production test proved that it is technically feasible to harvest gas from high concentration gas hydrate reservoirs in permafrost regions and it offered promise for full-fledged production in the future.

However, a recent drilling effort, the Hot Ice No. 1 well located in North Slope of Alaska as part of a two-year cost-shared partnership between the U.S. Department of Energy’s Office of Fossil Energy, Anadarko Petroleum Corp., Maurer Technology Inc., and Noble Engineering and Development, did not find gas hydrates as predicted, even though large gas shows were encountered.[26] This demonstrates that understanding of gas hydrate formation and distribution mechanisms is greatly needed for successful future explorations.

2.2.2 Flow Assurance
Free water and light hydrocarbons like methane frequently coexist during oil/gas productions, especially as the field matures. Some indigenous components of condensate or crude oil are also hydrate formers\textsuperscript{[27]} (Table 2.2\textsuperscript{[28]}). Deep-water operations and some land operations unavoidably encounter high pressures and moderately low temperatures due to harsh surrounding environments, which put the operating conditions well into the hydrate stability regions. Therefore, gas hydrates can form and agglomerate into hydrate plugs in the pipelines. Because the physical and mechanical properties of gas hydrates are similar to ice, i.e., solid, hard, and denser than typical hydrocarbons, the hydrate plugs interrupt normal operations by stopping the flow and can take days or months to dissociate, posing great economic loss and hazardous working conditions. Hydrate plug formation in long and often sub-seafloor flowlines are even more disastrous because it is a challenge just to accurately locate the hydrate blockage. Therefore, development of a hydrate prevention strategy is a crucial part of all deepwater projects. Oil/gas producers take every necessary step to ensure that operations in deep water remain free of hydrate plugs during normal production and shut-in/restart.\textsuperscript{[29]}

To design an effective strategy to prevent hydrate blockage, a combination of pipeline insulation and hydrate inhibitor injection is often considered. Hydrate prevention is usually expensive both in capital expenditure and operating cost. At current oil/gas production rates, the petroleum industry is spending more than a million US dollars per day on injecting hydrate inhibitors into the production/transmission lines.
<table>
<thead>
<tr>
<th>Natural Gas</th>
<th>Co-condensates/Oils</th>
<th>Process Inhibitors</th>
<th>Aqueous Phase</th>
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<tr>
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<td>Benzene*</td>
<td>Ethylene</td>
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<td>Propylene</td>
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<td>Hydrogen Sulphide</td>
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<td>Adamantane*</td>
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* Requires presence of smaller ‘help’ molecule to stabilise structure.

Table 2.2 Molecules identified as hydrate formers.

Three types of hydrate inhibitors are available to oil/gas producers for hydrate control: thermodynamic inhibitors, kinetic hydrate inhibitors (KHI), and anti-agglomerant hydrate inhibitors (AAHI). They differ by the purported mechanisms by which they address hydrate problems.

Thermodynamic inhibitors, like methanol and ethylene glycol, prevent hydrate formation by shifting the hydrate equilibrium curve toward higher pressures and lower temperatures, so that the operating condition is outside the hydrate stability region. On a molecular scale, these chemicals distort the water hydrogen-bonding
network, making it harder for water molecules to rearrange into clathrate structures. Thermodynamic inhibitors have been in application for over half a century. Their robust and effective performance has long been proven by a track record of successful case histories. Well-understood thermodynamic models and programs are available for accurate prediction of the amount of thermodynamic inhibitor needed for effective hydrate prevention. However, they normally have to be added at concentrations as high as 60% in the water phase. As the operation moves into deeper water, the subcooling gets higher, and so does the required volume of thermodynamic inhibitors. This leads to increased operating and capital expenses (OPEX and CAPEX, respectively) for field development, as well as logistical problems in remote and offshore applications. Release of production water containing thermodynamic inhibitors is harmful to the environment. Furthermore, because methanol can poison refinery catalysts, the presence of methanol in crude is undesirable for refineries and might impact the value of the produced crude. These drawbacks drive the industry to find alternatives to thermodynamic inhibitors, which eventually led to the emergence of low dosage hydrate inhibitors (LDHI), KHI and AAHI.

KHI is water-soluble polymers that have functional groups that can be accommodated into clathrate hydrate cages. Unlike thermodynamic inhibitors, they do not change the hydrate equilibrium curve, but significantly delay the hydrate nucleation and/or growth, so that the induction time is longer than the residence time of the fluids in the flowlines. In field applications, a small dose rate of KHI has been shown to significantly reduce the methanol consumption. Kinetic inhibitor molecules
work by interfering with the nucleation of the hydrate cage structures. They also adsorb onto hydrate micro-crystal surfaces probably because some of their functional groups can fit into certain clathrate cages in the hydrate lattice. Consequently they prevent rapid hydrate growth by distorting the regular hydrate crystal structure. The time length that KHI can keep the system hydrate free depends on the KHI concentration and subcooling. Higher KHI concentration increases the delay time, while higher subcooling shortens it. The applicability of KHIs is limited by the maximum system subcooling because, beyond a certain point, KHIs cease to be effective. The first generation KHI is able to withstand approximately 15°F subcooling. The capability of second generation KHI increased to 20°F subcooling. Once KHIs start to fail, hydrate formation is catastrophic and often results in a hydrate blockage.\textsuperscript{[29]} For these reasons, KHI is not an ideal choice during long-term production shut-in when the system is inside the hydrate formation region.

AAHIs are polymers that have both hydrophilic and hydrophobic ends, with the hydrophilic heads absorbed onto the hydrate crystal surface and the hydrophobic tails dissolved in the hydrocarbon phase. Like KHIs, AAHIs do not change the thermodynamics of the system. Even though some of AAHIs can function as kinetic hydrate inhibitors, they do allow hydrate to form but keep the hydrate crystals dispersed in the hydrocarbon phase so that they do not agglomerate into hydrate plugs. Hydrate crystals are then transported as a slurry in the hydrocarbon flows. Therefore AAHIs do not have the maximum treatable subcooling limitation and their effectiveness is not restrained by the length of time period. Unlike KHIs, AAHIs need
a continuous hydrocarbon phase to be effective. Systems with high water cuts (above 60%) are treacherous for AAHI application. To be most effective, LDHI (AAHI or KHI) must be introduced ahead of the potential hydrate point in subsea flowlines so that proper mixing is available to distribute the LDHI in the produced fluids. Even though some AAHIs actually improve water/oil separation, some of them can lead to emulsion formation and increased oil/water separation costs.

2.2.3 CO₂ Sequestration

It has been predicted that the concentration of CO₂ in the atmosphere will double within the next century if nothing is done to prevent this. Consequently the earth’s surface temperature would rise 2.0 – 4.5 °C, which would melt the Antarctic polar icecap with a subsequent ~50cm sea level increase. Other unknown environmental and health problems could also occur.⁴¹ One recent interesting observation is that CO₂ can efficiently displace CH₄ from methane hydrate at no thermal cost.⁴², ⁴³ Smith and Seshadri⁴⁴ also showed that the conversion of methane hydrate into carbon dioxide hydrate in porous media is thermodynamically favored. This opened the possibility of exploiting hydrated natural gas by sequestrating liquid CO₂ into hydrate reservoirs beneath the ocean floor.⁴⁵

2.2.4 Global Climate and Sea Floor Stability

The main component of naturally occurring hydrates, methane, is a very strong greenhouse gas, 24 times stronger than CO₂.⁴⁶ Methane hydrate deposits represent a dynamic system that is an important part of the continuous flowing global carbon cycle.⁴⁷ The release of methane into the atmosphere from the hydrate
reservoirs would result in significant global temperature increases, which would induce more hydrates to dissociate.\textsuperscript{[36]} From the record of $^{13}$C, it was suggested that the Late Paleocene thermal maximum was caused by a voluminous release of methane from hydrate reservoirs,\textsuperscript{[5]} which had a great impact on the evolution of life species on Earth. During future commercial methane hydrate explorations, the prevention of an extensive methane release from hydrate reservoirs into the atmosphere is very important to maintain the global climate stability.\textsuperscript{[38]} Furthermore, the dissociation of hydrates under the sea floor will create an over-pressurized fluidized layer at the base of the hydrate zone, which may trigger landslides.\textsuperscript{[39]} Geological records reveal that many sea floor stability failures concur with the hydrate instability zones of hydrate reservoirs. Petroleum drilling and production activity can destroy the stability of gas hydrates under the sea floor. Subsequent hydrate dissociation will cause sediment mobilization and represent a potential safety concern to such industrial operations.

\textbf{2.2.5 Gas Storage and Transportation}

Gudmundsson et al.\textsuperscript{[40]} demonstrated that structure II hydrate can be stored at $-15^\circ$C under atmospheric pressure for 15 days, retaining almost all the gas. Combination of this hydrate property with the fact that one cubic meter of fully occupied gas hydrate can contain up to 180 m$^3$ of natural gas (STP) leads to the proposal of employing gas hydrates as a novel media for natural gas storage and transportation. One distinct advantage this technique is its safety compared to liquefied natural gas (LNG) method. In case of tank ruptures, liquefied natural gas
usually would cause a blast and fireball, but if the gas is stored in hydrates, explosion won’t occur because of the limitation of the hydrate dissociation rate.[4]

Gas produced from remote locations far away from an existing gas pipeline and where a gas pipeline cannot be built and operated economically, is referred as stranded gas. In some cases, the stranded gas reserves are too small to justify a liquefaction facility. Because of the commercial value of stranded gas, methods are being sought to bring this gas to market. Gudmundsson and Borrehaug[41] have suggested that it is economically feasible to transport stranded gas in the form of gas hydrates. Their study also illustrated a substantial cost saving (24%) for the transport of natural gas in hydrates compared to liquefied natural gas from the northern North Sea to Central Europe.

However, industrial applications of hydrate storage/transportation processes are troubled by problems such as slow formation rates and unreacted interstitial water as a large percentage of the hydrate mass. Therefore, research efforts have been devoted to the development of techniques and chemicals that promote and expedite hydrate formation and improve hydrate storage capacity in a quiescent system.[42]

2.2.6 Others

Gas hydrates also have been proposed as potentially useful in novel gas separation processes,[43] desalination of seawater,[44] and the recovery of contaminants from groundwater.[45] Needless to say, the future of gas hydrate research and development is full of promises.
Chapter 3. Key Challenges

As summarized in the last chapter, the importance of gas hydrates has been realized in many applications. There are several outstanding research areas that are critical to the advancement of hydrate technologies.

3.1 Molecular Mechanisms of Hydrate Formation and Dissociation

Understanding hydrate formation and dissociation processes on a molecular level is an important step in mastering gas hydrate phenomena. Without this level of understanding, all the hydrate technologies would be only empirical and breakthroughs would be difficult. Consequently, their effectiveness and accuracy would be limited.

The failure to find gas hydrates as predicted in the Hot Ice No.1 well demonstrates the need for a more complete understanding of hydrate formation mechanisms. Scientists were perplexed by the absence of gas hydrate in the hydrate stability zone in spite of the coexistence of gas and free water. Fundamental research on hydrate mechanisms is greatly needed to explain and quantify such observed phenomenon. Better understanding will avoid drilling "dry holes" in the future and is the only way to confidently predict hydrate distributions in nature, the first step in commercially producing hydrated gas in large scale for sustaining an energy dependent world economy.

Designing effective low dose rate hydrate inhibitors for assuring hydrate plug free uninterrupted oil/gas production and transmission mandates a thorough understanding of hydrate molecular mechanisms because those chemicals are purported to interfere with hydrate formation processes on a molecular scale. As
oil/gas production moves into deeper water, low dose rate hydrate inhibitors may be the only alternative for treating hydrate problems in flow assurance because the required amount of thermodynamic inhibitors can increase to the point where it is logistically very difficult to manage the hydrate treatments. Current low dosage hydrate inhibitors are classified as kinetic hydrate inhibitors and anti-agglomerant hydrate inhibitors. As mentioned in the last chapter, kinetic inhibitors function by significantly delaying the hydrate nucleation point and slowing down the formation kinetics once hydrate starts to nucleate. Anti-agglomerant hydrate inhibitors prevent hydrate plug formation by dispersing small hydrate crystals in the hydrocarbon phase. Even though both classes of hydrate inhibitors have enjoyed certain degree of successful applications in the field, each of them has fundamental limitations. Because the design of those hydrate inhibitor chemical structures is only based on unproven conceptual hydrate formation pictures, accurate understanding of hydrate molecular mechanisms may yield new revolutionary chemicals for treating hydrate problems in flow assurance.

Unlike hydrate inhibitors in flow assurance, certain hydrate promoters are needed to promote and expedite hydrate formation in maturing the techniques of using clathrate hydrates for gas storage and transportation in order to overcome the limitation of slow reaction rates and incomplete reactions. Without understanding hydrate formation process on a molecular scale, the process of searching for effective hydrate promoters is bounded to be the time and effort consuming trial-and-error investigative path, instead of efficiently designing chemical structures from a bottom-up approach. This would certainly hinder the industrialization process of
hydrate storage/transportation technology and consequently delay the utilization of stranded gas by this energy-hungry society.

3.2 Gas Hydrate Behavior in Black Oil

Oil production in deep water are often troubled by hydrate formation because free water and light hydrocarbons often coexist in pipelines. Capital cost expense (CAPEX) and operating expense (OPEX) for hydrate treatment strategy are critical part of considerations during the appraisal stage of ultra deep-water projects. Those expenses largely depend on the system subcooling predicted by the hydrate phase diagram. However, current programs for predicting hydrate phase behavior are known to be inaccurate for hydrate in black oil systems. Erroneous predictions may not only involve extra unnecessary expenses that can kill the economical feasibility of a project but also pose the risk of plugging up operating pipelines that lead to production loss and expenses for treating the hydrate plugs.

All the current hydrate models require experimental data from a hydrocarbon and water mixture with known composition to “tune” the model parameters. However, accurate experimental data are scarce for hydrates in black oil, mainly due to the fundamental limitations of the traditional technique for measuring hydrate behavior in black oil. Therefore, there are great economical and safety motivations to develop innovative techniques for accurately acquiring hydrate data in black oil, not only to better manage a specific production location, but also to accurately predict hydrate information in other types of oils. Prior to the work reported in this thesis, no technique was capable of direct and accurate measurement of hydrocarbon hydrates in black oil.
Chapter 4. Literature Review

Since their practical applications have been long recognized, a rich collection of literature is available on various aspects of gas hydrates, especially regarding hydrate structures and thermodynamics. Because of the special importance of the key challenges laid out in the last chapter, a selective review of the previous work in these areas is necessary to put the current problems facing hydrate researchers into perspective and coach future research efforts into more productive investigative paths.

4.1 Molecular Mechanisms of Hydrate Formation and Dissociation

The first proposed hydrate formation and dissociation mechanisms were published by Sloan. In this conceptual picture of hydrate nucleation at a molecular level, Christiansen and Sloan\cite{47} suggested that before the formation of gas hydrates, the water molecules around the dissolved gas molecule form clathrate-like labile clusters, the so called hydrate precursors. Under proper thermodynamic conditions, hydrate precursors will agglomerate by sharing faces. When a precursor agglomerate reaches a critical size, gas hydrate will grow monotonically (Figure 3.1). If a heating process follows the end of hydrate formation, the hydrates will dissociate back to the liquid phase. Although no visual hydrate crystals remain, residual hydrate cage clusters still persist in the liquid water. Only after long periods of time, the clusters would be dispersed to a more normal water distribution.
Figure 3.1 Overview of hydrate formation hypothesis.
This gas hydrate mechanism proposition generated many controversies, focusing on the structure of water molecules around the non-polar solute (precursor hypothesis) near or during hydrate formation conditions and the existence of residual structures in the liquid phase after hydrate dissociation (post-cursor hypothesis).

4.1.1 Precursor Hypothesis

Hydrophobic hydration describes the hydration of non-polar molecules in water. Since the structure of the hydration shell around the non-polar solute is of special importance in understanding the mechanism of hydrate formation and evaluating the validity of the precursor hypothesis, a relevant literature review on this subject from the standpoints of theory, molecular simulation and experimental work is presented below.

4.1.1.1 Theory

Two concepts dominate in the theoretical research on the hydrophobic effect: the clathrate cage model and the cavity model,\[^{48}\] which are based on different views of water structures around apolar solutes.

The clathrate cage model suggests that water molecules form a clathrate-cage-like structure around non-polar solute molecules, which causes a large unfavorable entropic effect. Eley\[^{49}\] proposed an aqueous solubility theory for inert gases, in which at low temperature the solute remains in the cavities formed by hydrogen-bonded water with tetrahedral coordination. This theory can physically explain several phenomena associated with dissolution of inert gases, including the anomalously large negative solvation entropy. Based on the unusual entropy change, Frank and Evans\[^{50}\] suggested that the water is highly ordered around the non-polar
solute, forming frozen patches or microscopic icebergs. Claussen and Polglase\textsuperscript{[51]} interpreted the entropy loss for gas dissolution in water as the creation of clathrate water cages around the non-polar gases, which are the same structures as those in gas hydrates. Glew\textsuperscript{[52]} noted that the heat of dissolution of ten hydrate formers was very similar to the heat of hydrate formation from gas and ice, then claimed that the water molecules maintain maximum hydrogen bonds by aligning themselves around the solute to form clathrate structures, but that the water molecules in these structures are not as rigid as in gas hydrates. Lekvam and Ruoff\textsuperscript{[53]} developed a model based on the assumption that hydrate precursors exist in solution before formation of gas hydrates. Calculated model results quantitatively reproduced the experimental hysteresis curve.

In contrast to the clathrate-cage model, the cavity-based model states that formation of cavities rather than change in water structure around the non-polar solute is the predominant reason for the hydrophobic effect. Creation of cavities by the solute limits the volume of the translational motion of the solvent, which is responsible for the unfavorable entropic effect. Peirotti\textsuperscript{[54-56]} demonstrated that the scaled particle theory (SPT) could be successfully applied to predict the hydrophobic solvation free energy. This theory only includes the molecular size, density and pressure of water as input parameters. It does not explicitly account for any special hydrogen bonding structures. Ashbaugh et al.\textsuperscript{[57]} extended a recent microscopic model for associating fluids\textsuperscript{[58]} to aqueous solutions with non-polar species. In this approach, although aqueous hydrogen bonding is explicitly considered in a
simplified way, no specific water structure around the non-polar solutes needs to be invoked to successfully capture the solvation properties of water.

These two theories, based on totally different concepts, both successfully explain some thermodynamic properties of apolar gases in aqueous solution. This contributes to the belief that the ability of a theory to explain a phenomenon does not prove the validity of what the theory states. Theory alone cannot give a definitive molecular picture for the hydrophobic solvation process.

4.1.1.2 Molecular Simulation

Molecular simulation generates voluminous literature on the molecular detail of hydrophobic hydration. A vigorous debate centers on whether the presence of non-polar molecules structures nearby hydrogen bonding network.

Structure creation argument:

Some research efforts support the idea that insertion of a non-polar molecule into water phase creates a structured clathrate-like structure around it. From a Monte Carlo simulation of a dilute aqueous solution of methane at 298K and 1atm, Owicki and Scheraga\textsuperscript{[69]} detected lower and more sharply distributed nearest-neighbor and binding energies in the first hydration shell which contains \(\sim 23\) water molecules. From a similar simulation, Swaminathan et al.\textsuperscript{[60]} concluded that a distorted defective continuum pentagonal dodecahedral clathrate structure exists around the methane solute with a stronger hydrogen bonding compared to bulk fluid.

Geiger et al.\textsuperscript{[61]} carried out molecular dynamics simulation of the hydration of Lennard-Jones solutes. They found that the orientational structure of water cages surrounding the solutes is comparable to clathrates. Through a simulation of
temperature dependence of the hydrophobic hydration, Guillot and Guissani\textsuperscript{[62]} showed that solute-water pair distribution function at room temperature is very similar to those in clathrate hydrates. Below the water boiling temperature, a polyhedral cage forms around the solute causing the negative entropic effect. This cage structure is destroyed as temperature increases to a certain value. The computer simulation results from Chau and Mancera\textsuperscript{[63]} revealed an increase in water structure around methane with increasing pressure but the opposite is observed in the bulk phase.

Long and Sloan\textsuperscript{[64]} simulated water clusters around apolar solutes using molecular dynamics. Their results showed that the water clusters resemble hydrate-like labile cavities with a quantized coordination of modulus four. Skipper\textsuperscript{[65]} and Mancera\textsuperscript{[66]} utilized molecular dynamics to investigate the methane-water solution. Water molecules reorganize around a methane molecule forming a clathrate-like cage in order to attain maximum hydrogen bonds. The hydrophobic attraction between methane molecules increases with temperature, which agrees with previous hydrophobic theory.\textsuperscript{[67]} Using a simple statistical mechanical water model, Silverstein et al.\textsuperscript{[68, 69]} found that a non-polar solute causes ordering and strengthening of hydrogen bonds in the first hydration shell in cold water; the opposite occurs in hot water.

Computer simulation works of hydrophobic hydration by Mancera\textsuperscript{[70]} and Lazaridis\textsuperscript{[71]} showed a structured hydration around non-polar solutes compared to the bulk phase at moderate temperatures. Hirai et al.\textsuperscript{[72]} simulated the dissolution process of CO\textsubscript{2} in water under pressurized condition. It was demonstrated that water
forms a characteristic cage structure of type I clathrate around CO₂ guest molecules after 260 ps. Guo et al.⁷³ calculated the lifetime of different types of cage-like water clusters with or without a methane molecule inside after inserting them into liquid water. It was concluded that the inclusion of methane molecule increases the lifetime of the cage-like water cluster and the authors argued that this finding supports the hydrate precursor hypothesis.

No structuring effect argument:

However, several groups argued that the non-polar solutes do not increase the structure of water. Meng and Kollman⁷⁴ performed molecular dynamics simulations to evaluate the properties of water around some organic solutes at P ≈ 1 bar and T ≈ 300 K. From the water binding energies, water polarization, and water-water hydrogen bonding data, they concluded that water structure around hydrophobic groups is preserved rather than increased. Hernandez-Cobos et al.⁷⁵ investigated the temperature dependence of the hydrophobic hydration of methane from a histogram re-weighting Monte Carlo simulations. By calculating oxygen-oxygen radial distribution functions of pure water and of the first hydration shell for water/methane mixture, they observed that the structure of water is hardly changed by the insertion of methane. From the decrease of water-water binding energy, they inferred that the water structure after hydrophobic solvation of methane should be more disordered and the unfavorable entropic effect can be explained solely by excluded volume effect. This contradicts to the concept that water forms clathrate-like cages around non-polar solutes.
This inconsistency from simulation results manifests the complexity of the system and difficulty in interpreting the results.

4.1.1.3 Experimental Work

Due to the extremely low solubility of non-polar species in water, high sensitivity experimental techniques are necessary to reveal molecular details of hydrophobic hydration. NMR, neutron diffraction, X-ray, and Raman are the most widely employed techniques.

NMR:

Using $^1$H spin-echo NMR technique, Haselmeier et al. investigated aqueous solutions of xenon in the temperature range from 273 to 333K at pressures up to 6Mpa. Reorientational correlation time and self-diffusion coefficients of water in the first hydration shell show retardation effects compared to the bulk water phase, implying an increased water structure near xenon. Nakahara and Yoshimoto also found the same effect by measuring NMR rotational correlation time of D$_2$O in dilute aqueous solutions of benzene. They also found that this effect is enhanced in super cooled solutions. Nakahara et al. suggested that the rotational dynamics of water molecules positively correlates with hydrogen bonding strength. By examining the temperature dependence of the rotational mobility and the effective volume of benzene, they concluded that a clathrate-like cage is formed around benzene even before clathrate hydrate formation.

Neutron Diffraction:

Neutron diffraction was utilized by Broadbent and Neilson to probe the inter-atomic structure of argon in water. They detected a well-defined argon
hydration shell composed of 16(2) water molecules. Applying the same practice to hydrophobic hydration of methane, De Jong et al.\(^{[80]}\) reported that a methane molecule is surrounded by a shell containing 19(2) tangentially orientated water molecules. Koh et al.\(^{[7]}\) kept track of water ordering around methane during hydrate formation by neutron diffraction with isotropic substitution. Their results showed that a loosely ordered hydration shell forms around methane in the liquid phase. This structure becomes subtly more disordered during hydrate formation but changes dramatically once hydrate forms. However, neutron experiments of alcohol aqueous solutions from Turner and Soper\(^{[81]}\) showed no enhancement of water structure compared to pure water.

**X-Ray:**

By taking advantage of extended X-ray absorption fine structure spectroscopy, Filipponi et al.\(^{[82]}\) explored the structure of the hydrophobic hydration shell of Kr in the pressure range of 20 to 100 bars and at a temperature of 320K. The Kr-O partial distribution function extracted from experimental data revealed the existence of a well-defined hydration shell around Kr, with a hydration number around 20 water molecules. They\(^{[83]}\) further tracked the transition from liquid solution to solid state and then compared the Kr hydration shell structure in liquid and in clathrate hydrate phases. Using Kr-O radial distribution functions, they demonstrated the formation of a hydration cage around Kr in aqueous solution, with the size comparable to that of small cages in hydrates, but more loosely defined. In an *in situ* X-ray study of Xe and Kr hydrate formation, Montano et al.\(^{[84]}\) identified a cage-like water complex around
Kr, which may act as hydrate precursors. When temperature decreases, those cages are assumed to interact with each other to form clathrate hydrate.

*Raman:*

Subramanian and Sloan\textsuperscript{[85]} used time-resolved Raman to scrutinize the transformation of methane aqueous solution to methane hydrate. The measured spectra showed a smooth transition during this process, indicating that hydrate precursors might preexist hydrate formation. Nakano et al.\textsuperscript{[86]} detected that Raman shifts of the CO\textsubscript{2} molecule dissolved in the water phase are very close to those of CO\textsubscript{2} in the hydrate phase. It was argued that some hydrate-like structures exist in the water phase; that is, the structure of water around CO\textsubscript{2} in the aqueous solution is similar to that of the hydrate cage.

**4.1.2 Post-cursor Hypothesis**

After dissociation of gas hydrates, Sloan\textsuperscript{[1]} speculated that the partial clathrate cage structures, i.e., post-cursors, still persist in solution until up to high temperatures. Thus, reformation of gas hydrates from "hydrates melt" requires less super-cooling and less induction time. This is the so-called *memory effect*, first identified by Bishnoi\textsuperscript{[87]} The idea of residual structure has important implications for the gas industry. For example, removal of water should follow dissociation of hydrates plugs. Otherwise the residual structure will enable rapid reformation of solid hydrates in the pipelines.

However, the past work shows controversial opinions about hydrate residual structure after hydrate dissociation.

*Evidence in Favor of Residual Structure:*
Sloan et al.\textsuperscript{[88]} measured the viscosity of water before hydrate formation and after dissociation. The viscosity measured before hydrate formation is regarded as a baseline. As the hydrate formed, the apparent viscosity increased sharply. Then the temperature was increased to dissociate the gas hydrate until no visual hydrate crystal remains in solution. However, the viscosities did not decrease to the baseline until after the solutions had been heated to 28 °C and allowed to mix for approximately 24 hours. This residual viscosity was attributed to residual clathrate structure after hydrate dissociation. Because the heat of melting ice is only 13 percent of the sublimation energy of solid ice, Stillinger\textsuperscript{[89]} concluded that most hydrogen bonds survive after melting, which suggests some clathrate-like hydrogen bonds may also survive after hydrate dissociation.

Takeya et al.\textsuperscript{[90]} measured the times to nucleate CO\textsubscript{2} hydrates using water subjected to different treatments. Water from previously formed ice nucleated at a significantly increased rate, showing a freezing-memory effect. This effect vanished when the melt water was heated to 298K before nucleation. In the study of dissociation and reformation of methane hydrate crystals by Raman spectroscopy, Ohgaki et al.\textsuperscript{[91]} found that as thehydrate dissociates to liquid water, the C-H (methane) and O-O (water) Raman wave numbers stay essentially unchanged. Thus, cage structures around methane may persist even after no visual hydrate crystal remains.

\textit{Evidence in Odds with Residual Structure:}

In contrast to the residual structure concept, Benmore and Soper\textsuperscript{[92]} failed to notice through neutron diffraction significant structural differences between
tetrabutylammonium chloride aqueous solutions subjected to different thermal treatments. Uchida et al.\cite{93} decomposed and reformed CO$_2$ hydrate through temperature and pressure changes. The memory effect was reproduced only through temperature changes, not through pressure changes. They proposed that the memory effect probably did not come from the residual structure in solution but can be explained based on CO$_2$ concentrations remaining in solution after hydrate dissociation.

4.2 Gas Hydrate Behavior in Black Oil

Study of gas hydrates in black oil is difficult because visual observation of hydrate crystals is not possible and the gas diffusion rates are slow in a viscous oil phase, which makes it difficult to measure accurate hydrate equilibrium points by monitoring pressure change. It can take up to 24 hours for the gas phase and liquid phase to reach equilibrium.\cite{48} Even though it has been widely recognized that gas hydrate behavior in black oil is poorly understood, only limited amount of literature has touched on this topic. No kinetic data on gas hydrates in black oil has been reported.

Current hydrate equilibrium prediction programs, mainly based on the statistical thermodynamics framework on clathrate hydrate developed by van der Waals and Platteeuw,\cite{94} frequently produce erroneous results for hydrate behavior in black oil. Notz et al.\cite{95} performed hydrate predictions for a black oil system using several commercial hydrate programs, HYSIM, PROCESS, PIPEPHASE and EQUIPHASE. The predicted equilibrium pressures at some temperatures could be different from experimental data by as much as 2000 psi. The error range became
even larger if hydrate inhibitors were included. Attempts were made to "tune" the models by varying binary interaction parameters and properties of the heptane plus fractions, which yielded little improvement on the hydrate equilibrium prediction results. Hopgood\textsuperscript{[9]} used an in-house hydrate prediction model to calculate the hydrate equilibrium condition for the same system studied by Notz. Results showed that the predicted hydrate P-T curves were displaced to lower temperatures from the experimental data by 6-7 °F.

The errors associated with hydrate predictions in black oil systems could cause significant cost implications. An uncertainty of \textasciitilde 10 °F can dramatically increase the capital cost for designing a subsea production system. Possible sources of error were attributed to:\textsuperscript{[96]} (1) an inaccurate prediction of they hydrocarbon fugacities due to incompletely characterized petroleum fractions, (2) inaccurate aqueous phase activities, or (3) faulty hydrate structure predictions.

In order to develop a hydrate model that can produce reliable predictions, quality experimental data are need within 1-2 °F uncertainty.\textsuperscript{[46]} Because the nature of black oil deters direct visual observation, traditional experimental methods to gather hydrate data in black oil have frequently depended on monitoring system pressure changes. In this method, water, black oil, and gas are charged into a high-pressure cell. The pressure is monitored as this closed system is ramped in temperature. Because the gases have to transport through the liquid oil and water phases, some means of mechanical stirring are often employed to facilitate the gas mass transfer. Pressure drops dramatically upon hydrate formation because hydrate formation consumes large quantity of gas. After hydrate formation, the temperature
is raised to dissociate the hydrate. As hydrate dissociates, gases are released and pressure increases significantly. The transition point that indicates complete hydrate dissociation, (normally where pressure and temperature return to the original P, T curve before hydrate formation), is identified as the hydrate thermodynamic point.

Shukla and Kalpakci\textsuperscript{[48]} employed this technique to measure the hydrate equilibrium lines in black oils using an autoclave device at Westport. They reported that this measurement was a difficult task because it could take up to 24 hours for the gas and liquid phases to reach equilibrium. This delay may result in several degrees of error in measurements. Ivanic et al.\textsuperscript{[96]} modified this method a little by cycling through hydrate formation and dissociation several times in order to make the temperature ramping loop smaller and more accurately locate the hydrate equilibrium point. However, the mass transfer rate limitation of gas in oil phase cannot be eliminated by this improvement, which impedes equilibrium from being quickly established.

No hydrate kinetic measurement in black oil has ever been attempt because the traditional pressure monitoring technique cannot accurately quantify hydrate formation and dissociation due the small gas diffusion rates in oil phase mentioned earlier. A technique that can directly observe hydrate behavior in black oil is in great need.
Chapter 5. Research Overview

Review of previous clathrate hydrate literature demonstrates that clear understanding of hydrate molecular mechanisms and techniques for gathering accurate gas hydrate information in black oil are not available. This chapter details the research undertaken in this work on these areas, which advancements of hydrate technologies with practical importance heavily depend on.

5.1 Molecular Mechanisms of Hydrate Formation and Dissociation

As discussed in Chapter 4, the nature of hydrate molecular mechanisms has been pursued vigorously through theory, simulation, and experiment. However, a clear picture of the molecular process of hydrate formation and dissociation is still far from complete. Regarding the formation hypothesis proposed by Sloan, theories and simulations yielded conflicting results on the existence of hydrate precursor, the crucial assumption that determines the validity of the proposed mechanism. Experimental works revealed structured hydration shells around the dissolved non-polar hydrate formers, but the organization of their hydrogen bonds is less ordered than that in hydrate phase and the number of water molecules involved in each hydration shell is also different from that in a clathrate cage.

Studies of molecular hydrate mechanisms present great experimental challenges due to low concentrations of gases in water and the high pressures involved. Experiments usually require specially designed sample cells and high sensitivity instruments capable of providing structural information on a molecular scale.
Nuclear Magnetic Resonance (NMR) Spin-Lattice Relaxation Time ($T_1$) and Spin-Spin Relaxation Time ($T_2$) measurements have been shown to be powerful techniques in studying micro-dynamic behavior of liquids and therefore providing local molecular level structural information surrounding the NMR responsive guest molecules.\textsuperscript{[10]} Magnetic Resonance Imaging (MRI) can non-invasively and accurately capture the hydrate formation and dissociation patterns. (A chapter of background knowledge on NMR/MRI can be found in the Appendix A).

THF and water form structure II hydrate at \(~4.5\, ^\circ\text{C}\) under ambient pressure.\textsuperscript{[97]} It is a good model system with which to study clathrate hydrate mechanisms because its formation condition is mild and THF is miscible with water at conditions of interest.

Therefore, the following research using NMR/MRI were undertaken:

- Measured $T_1$ and $T_2$ of THF in D$_2$O as a function of temperature before hydrate formation to probe the existence of hydrate precursors by calculating the rotational activation energies.

- Monitored $T_1$ and $T_2$ of THF in liquid or solid phases during hydrate transition to investigate the fluid structure that is coexisting with solid hydrate phase, in order to gain understanding of hydrate formation and dissociation process.

- Measured $T_1$ and $T_2$ of THF in D$_2$O as a function of temperature after hydrate dissociation and compare them with those before hydrate formation to evaluate the existence of hydrate post-cursors.

- Acquired hydrate formation/dissociation patterns using MRI.
Sloan\cite{88} attributed the residual viscosity after gas hydrate dissociation to the existence of residual clathrate structure in solution. However, it is well known that the gas concentration is very high immediately after hydrate dissociates into the liquid phase and the diffusion fluxes of non-polar molecules in water are very small. Therefore, it is not clear whether the observed residual viscosity is caused by residual clathrate structure or excess amount of dissolved gas.

THF is miscible with water at the same molar concentration as solid THF hydrate;\cite{98, 99} thus experiments can be performed at constant concentration before, during, and after hydrate formation. To eliminate the complication of mass transfer phenomenon on the experimental results by Sloan and obtain a better understanding of the residual hydrate structure hypothesis, the following research on residual viscosity was performed:

- Measured the viscosity of THF:D$_2$O=1:17 (molar ratio) solution before hydrate formation and after dissociation using Champion Technologies Hydrate Rocking Cell (CTHRC) to detect the reported residual viscosity phenomenon.

5.2 Gas Hydrate Behavior in Black Oil

As explained in the last chapter, the traditional method to study gas hydrate phase behavior in black oil by measuring pressure and temperature has some inherent limitations due to small gas mass transfer rates in the hydrocarbon phase. To overcome these limitations, a method that can immediately detect and accurately quantify hydrate formation and dissociation in black oil is needed.
In a proton NMR spectrum, different hydrogen functional groups have different chemical shifts. The chemical shifts of water and saturated hydrocarbons, the dominant components in the black oil and natural gas, are about 3ppm apart.\textsuperscript{[100]} Thus, the water and oil components should be distinguishable in a high field NMR with sufficient magnetic field homogeneity. The water peak area in the NMR spectrum is directly related to the amount of liquid water in the sample. Because the free induction decay of water in gas hydrates at these fields is so short, and its spectral line is so broad, it ceases to contribute to the liquid water peak, and consequently the water peak decreases. Hydrate formation and dissociation should be able to be immediately detected and easily quantified from the changes of water peak area, instead of depending on pressure responses like in the traditional method.

Therefore, to evaluate the viability of employing proton NMR spectroscopy to directly and accurately observe in situ hydrate behavior in black oil, the following research was carried out:

- Performed proton NMR spectroscopy study of black oil / water mixture using an 85 MHz magnet, to determine if these constituents could be distinguished.

- Monitored hydrate formation and dissociation in black oil using proton NMR spectroscopy under high pressure.
Chapter 6. NMR/Viscosity Investigation of Clathrate Hydrate Formation and Dissociation*

6.1 Summary

To better understand clathrate hydrate mechanisms, nuclear magnetic resonance (NMR) and viscosity measurements were employed to investigate tetrahydrofuran (THF) hydrate formation and dissociation processes. In NMR experiments, the proton spin lattice relaxation time ($T_1$) of THF in deuterium oxide ($D_2O$) was measured as the sample was cooled from room temperature down to the hydrate formation region. The $D_2O$ structural change around THF during this process was examined by monitoring the rotational activation energy of THF, which can be obtained from the slope of $\ln(1/T_1)$ vs $1/T$. No evidence of hydrate precursor formation in the hydrate region was found. $T_1$ measurements of THF under constant subcooling temperature indicate that THF hydration shells do not undergo much structural rearrangement during induction. The $T_1$ of THF was also measured as the sample was warmed back to room temperature after hydrate dissociation. $T_1$ values of THF after hydrate dissociation were consistently smaller than those before hydrate formation and never returned to original values. It was proposed that this difference in $T_1$ after hydrate dissociation indicates that the THF-$D_2O$ solution is more microscopically homogeneous than before hydrate formation. In viscosity experiments, a Champion Technologies Hydrate Rocking Cell (CTHRC) was used to probe the residual viscosity phenomenon after Green Canyon (GC) gas hydrate as well as THF hydrate dissociation. The residual viscosity reported in the literature was

observed after GC hydrate dissociation but not after THF hydrate dissociation. Because GC hydrate behavior involves significant amounts of gas mass transfer while THF hydrate does not, one might conclude that the residual viscosity observed after GC hydrate dissociation was likely caused by the supersaturated gas concentration and its general effect on solvent viscosity, not necessarily by a clathrate water structure lingering from the solid.

6.2 Introduction

Since the first discovery that water forms clathrate hydrate with chloride in 1810 by Sir Humphrey Davy, about 200 years of research has been devoted to understanding hydrate phenomenon. This continuous effort well established the thermodynamic, physical, and structural properties of gas hydrates and provided a rich collection of hydrate formers. However, clathrate hydrate formation and decomposition mechanisms and kinetics are still far from clear due to a lack of appropriate experimental techniques capable of probing dynamic structural information on the molecular level. The actual formation and dissociation mechanisms have important impacts on all hydrate applications. Clarification of the formation mechanism is especially important for designing kinetic inhibitors or antiagglomerant hydrate inhibitors that are expected to intervene with the hydrate formation process on the molecular scale.

Current hypotheses[1] about hydrate formation and dissociation involve hydrate pre-cursor and post-cursor structures. The hypothesis states that, prior to hydrate formation, water molecules form individual clathrate cages (hydrate precursors) around the dissolved guest molecules with one guest molecule inside
each cage. Under favorable conditions, these cages will agglomerate and form solid clathrate hydrate. The hypothesis also states that upon melting, the solid hydrate phase dissolves into hydrate cage clusters. Those clusters, also known as residual structures or post-cursors, persist in the liquid phase over a long period of time provided the temperature stay within certain limits.\cite{101}

To understand hydrate formation and dissociation mechanisms, many researchers have studied hydrates with a particular emphasis on the pre-cursor and post-cursor hypotheses. Molecular simulations generated voluminous numerical data on the elemental molecular detail of hydrophobic hydration processes, which is important for evaluating the pre-cursor hypothesis. A vigorous debate continues on whether hydrophobic solutes structure the water molecules around them. One side argues that non-polar solutes enhance the order of the hydrogen-bonding network and create structured hydration shells around them.\cite{59-66, 68-70} On the other hand, some simulation results showed no indication of enhanced structure around hydrophobic solutes.\cite{71, 74} Even though computer simulation studies reached conflicting conclusions on whether non-polar solutes structure water network around them, they seem to all agreed that long-lived clathrate cages in solution do not exist. The orientation of hydrogen bonding in the hydration shell is the same as in hydrate clathrate cages, but the organization of the hydrogen bonds is less ordered and the number of water molecules in each hydration shell is also different from that in a clathrate hydrate cage. Experimental works have also been carried out to probe the water structures around dissolved non-polar solutes. Results seem to agree with those from computer simulation; that is, only loosely organized hydration cages form
around hydrophobic solutes, with no evidence of regular clathrate cages in solution.\textsuperscript{[7, 75, 79, 80, 82]}

The fact that no regular clathrate cages have been found in the water phase\textsuperscript{[102, 103]} before hydrate formation indicates that the actual hydrate formation process may be much more complicated than what the hypothesis suggests. Studies of molecular hydrate formation mechanisms present great experimental challenges due to low concentrations of gases in water and the high pressures involved. Experiments usually require specially designed sample cells and high sensitivity instruments capable of providing structural information on a molecular scale.

NMR $T_1$ measurement has been shown to be a powerful technique in studying micro-dynamic behavior of liquids\textsuperscript{[10]} and therefore providing local molecular level structural information surrounding the NMR responding guest molecules. THF and water form structure II hydrate at $\sim 4.5 \, ^\circ\text{C}$ under ambient pressure. It is a good model system to study clathrate hydrate mechanisms because its formation condition is mild and THF is miscible with water at conditions of interest. In this work, $T_1$ of THF in $\text{D}_2\text{O}$ was measured as the sample was cooled from room temperature to hydrate formation conditions in order to investigate the hydrate formation mechanism. This allowed us to monitor the structural change of the hydration shells around THF molecules as a function of temperature to and it gave a unique opportunity to examine whether hydrate precursors form under hydrate conditions.

The residual structure dissociation hypothesis is not as widely studied as the hydrate precursor hypothesis. It has been observed that reformation of gas hydrates from this "hydrate melt" requires less sub-cooling and less induction time. This
phenomenon is called the *memory effect*. Vysniauskas and Bishnoi\[^{87}\] proposed that it is the existence of residual clathrate structure in water after hydrate dissociation that is responsible for the memory effect.

More recently, Sloan et al.\[^{88}\] discovered that the viscosity of water after methane hydrate dissociation is initially higher than that before hydrate formation under the same pressure and temperature. The viscosity returns to normal only after a long period of time. This macroscopic residual viscosity phenomenon is argued as evidence of residual structure, clathrate aggregates remaining in water after gas molecules are released.\[^{15}\] However, it is well known that the diffusion rate of methane in water is very small. After hydrate dissociation, it is very likely there is still a large amount of methane dissolved in water solution due to mass transfer rate limitation. Since dissolved methane structures the hydrogen bonding network in water,\[^{104}\] water super-saturated with methane will have a higher viscosity than water simply saturated with methane under the same pressure and temperature. Therefore, it is not clear whether the observed residual viscosity is caused by residual clathrate structure or excess amount of dissolved methane.

To eliminate the complication of mass transfer phenomenon on the experimental results mentioned above and obtain a better understanding of the residual hydrate structure hypothesis, in this work we chose to study the possibility of residual viscosity after THF dissociation. THF is miscible with water at the concentration of solid THF hydrate;\[^{98, 99}\] thus experiments can be performed at constant concentration before, during, and after hydrate formation. Stangret and Gampe\[^{105}\] recently demonstrated that the hydrophobic hydration of THF dominates
over the hydrophilic hydration at low THF concentrations, including the hydrate composition, THF:H₂O = 1:17 (molar), and the water-THF hydrogen bonds are not very important for the fluid structure of dilute solutions. Therefore, in terms of water structure change, THF is not far from other non-polar solutes. Viscosity of the sample was monitored before hydrate formation and after dissociation using CTHRC (Figure 6.1) to detect the reported residual viscosity phenomenon. Since THF concentration in water is constant, if the residual viscosity phenomenon is observed, it would be a strong demonstration of the existence of residual clathrate hydrate structures, i.e., post-cursors.

Figure 6.1 Schematic of the Champion Technologies Hydrate Rocking Cell apparatus.
Fleyfel et al.\textsuperscript{[106]} combined macroscopic hydrate experiments (visual rocking cell) with microscopic hydrate experiments (NMR) to investigate clathrate residual structure at the point where hydrate particles become invisible. They found evidence that some clathrate cages still exist in solution after hydrates visually disappear. In this work, to investigate the molecular evidence of residual structure for THF hydrate, we measured $T_1$s of THF as a function of temperature after THF hydrate dissociation in the NMR experiment mentioned earlier. Results will be compared with that before hydrate formation to examine any difference caused by the history of hydrate formation.

6.3 Experimental Section

6.3.1 NMR Microscopic Measurements

6.3.1.1 Theoretical Background

Spin lattice relaxation mechanisms for THF are composed of two parts, intermolecular dipole-dipole and intra-molecular dipole-dipole interactions. When the THF to D$_2$O molar ratio is 1:17, (the same composition as in THF hydrate), most of the THF molecules are completely surrounded by D$_2$O hydration shells, and intra-dipole-dipole is the main spin relaxation mechanism. Orientational structures of D$_2$O in hydration shells have a direct impact on the rotational motion of enclosed THF molecules. Based on NMR theory,\textsuperscript{[107]} $T_1$ is inversely proportional to the rotational correlation time $\tau_c$. $\tau_c$ is usually believed to follow the Arrhenius behavior.

$$\frac{1}{T_1} \propto \tau_c$$  \hspace{1cm} (6.1)

$$\tau_c = \tau_o e^{E_a / RT}$$  \hspace{1cm} (6.2)
\[
\frac{d \ln \left( \frac{1}{T_2} \right)}{d \left( \frac{1}{T} \right)} = \frac{E_a}{R}
\]

(6.3)

Where \( \tau_0 \) is a constant pre-exponential factor; \( E_a \) is the rotational activation energy, a manifestation of hydration cage structure around THF, and not sensitive to temperature; T is temperature in Kelvin; R is the molar gas constant. Combining equations 6.1 and 6.2 yields Equation 6.3. Equation 6.3 says the slope of \( \ln(1/T_1) \sim (1/\text{temperature}) \) gives the rotational activation energy \( E_a \). Therefore, by tracking the changes in the slope of \( \ln(1/T_1) \sim (1/\text{temperature}) \), we can measure \( E_a \) and evaluate the changes in hydration shell structure around dissolved THF molecules as a function of temperature.

**6.3.1.2 Experimental Details**

\( T_1 \) measurements of THF (Aldrich, 99+% in D\(_2\)O (Cambridge Isotope Laboratories, D 99.9%) at various temperatures were performed on an 85 MHz Oxford horizontal 32 cm wide bore NMR with imaging capability, using a LITZ RF Volume Coil (with 14 cm internal diameter) from Doty Scientific, Inc (Figure 6.2). Data were acquired and processed using Varian VNMR software and INOVA hardware system. An Air-Jet temperature controller blew cold (dry) air to control sample temperature. It is capable of controlling temperature from \(-40 {^\circ}\text{C} \) to 100 \( {^\circ}\text{C} \) with \( \pm 0.1 {^\circ}\text{C} \) stability. A glass bottle with a cap that has a Teflon\textsuperscript{©} liner was used to contain the deoxygenated THF:D\(_2\)O = 1:17 (molar ratio) mixture. A LUXTRON\textsuperscript{©} fluoroptic thermometer was mounted into the glass container through the cap to monitor system temperature. Its output reading resolution is \( \pm 0.1 {^\circ}\text{C} \).
Since trace amounts of oxygen may alter $T_1$ of THF significantly, we deoxygenated pure $D_2O$ and THF liquids separately in Teflon containers by periodically flushing the gas above the liquid phase with pure nitrogen gas while periodically shaking the sample containers to facilitate oxygen to diffuse out of the liquid phase. After the gas phase had been flushed six or seven times over about 12 hours, THF and $D_2O$ were mixed on the molar basis of 1:17. All these processes were operated within a closed glove box with nitrogen environment. After allowing the sample to stabilize for half a day, we put the sample into the NMR probe for $T_1$ measurements. (The success of deoxygenation was demonstrated by that fact that after deoxygenation, $T_1$ increased about 2 seconds compared to the sample without deoxygenation). $T_1$s were measured using inversion recovery technique. All samples' $90^\circ$ and $180^\circ$ pulses were calibrated before every measurement. VNMR software, given inputs of possible minimum and maximum $T_1$ values, automatically generates standard $180^\circ-\tau-90^\circ$ pulse sequences with various values of $\tau$. It took 4~6 minutes to take a $T_1$ data point.

![Diagram](image)

**Figure 6.2** Schematic of the NMR experimental setup.
The sample was cooled from room temperature (\(\sim 25 \, ^\circ C\)) to sub-zero temperatures with an average cooling rate of \(\sim 0.5 \, ^\circ C/\text{hour}\) until hydrate formation happens. Hydrate formation was indicated by a jump in the sample temperature. Oyama et al.\textsuperscript{[108]} proposed that under hydrate condition, water around dissolved CO\(_2\) takes time to rearrange into individual clathrate cages before hydrate formation. To test this hypothesis, we measured \(T_1\) as a function of time while the temperature was kept constant in subcooling state. If the hydration shell structures around THF experience rearrangements, the \(T_1\) of THF would vary. After hydrate formation, temperature was raised to completely dissociate the hydrate. \(T_1\) was also measured as the sample was heated back to about 25 \(^\circ C\).

6.3.2 Viscosity Macroscopic Measurements

The viscosity experiments for THF (99+%, Aldrich) – Deionized (DI) water system were performed on the state of the art CTHRC, which is an apparatus with high-pressure sapphire tubes placed on a rack. It is capable of handling pressures up to 5000 psi. The rack is immersed in a temperature controlled thermal bath and it rocks \(\pm 45^\circ\) from horizontal position through a computer-controlled step motor. As the rack rocks, the ball inside the tube rolls from one end to the other and each tube functions like a rolling ball viscometer. The motion of the ball is detected through two sensors mounted on both ends of each tube. The time that the ball takes to travel from one sensor to the other is recorded as an indication of the fluid viscosity inside the tube. Changes of the fluid viscosity in the tubes can be sensitively detected by measuring the ball travel speeds. Hydrate formation is indicated by an increase in fluid apparent viscosity while system temperature and pressure are kept constant.
The ball can be eventually immobilized by the hydrate blockage. Hydrate onset is also detectable by visual observation of hydrate crystal deposit on the tube's inside wall. Ball travel time, temperature, and pressure data are collected every minute into a terminal computer using LabView®.

Green Canyon (GC) gas hydrate experiments were first performed on CTHRC to duplicate the residual viscosity phenomenon reported in the literature in order to assure that the rocking cell we use is sensitive enough. GC gas is composed of 87.2% (mol) CH₄, 7.6% C₂H₆, 3.1% C₃H₈, 0.8% n-C₄H₁₀, 0.5% l-C₄H₁₀, 0.2% n-C₅H₁₂, 0.2% l-C₅H₁₂, 0.4% N₂. Every tube was first charged with 9 ml DI water. After the system was purged three times with 50 psi GC gas, 1000 psi GC gas was introduced into the tubes. The pressure was kept constant at 1000 psi during the experiment. Once charged, the cell temperature was initially raised to 30 °C to eliminate any possible pre-existing extra structure in water. The system was then lowered to 20 °C and equilibrated for ~2 hours to establish a viscosity baseline at this temperature. The temperature was then further cooled down to 15 °C to initiate hydrate formation. The predicted hydrate equilibrium temperature by CSMHYD is 17.8 °C for this pressure and gas composition. To ensure complete hydrate formation, the temperature was lowered to 5 °C before it was raised to dissociate the hydrate. Then the system was slowly warmed back to 20 °C until complete hydrate dissociation occurred. The system was equilibrated to establish the viscosity baseline at this temperature again.

Viscosities of the THF-water system were measured in a similar fashion. DI water and THF were added in a H₂O:THF = 17:1 molar ratio, the composition in THF
hydrate. The tubes were then sealed and heated to 30 °C to eliminate any pre-existing extra structure in the water. The system temperature was then lowered to hydrate formation conditions. During this cooling process, the system was allowed to equilibrate at 10 °C and 6 °C for about 300 minutes in order to establish the viscosity baselines at these temperatures. After complete hydrate formation, the system was warmed up to dissociate the hydrate. The system was equilibrated again at 10 °C and 6 °C to establish the viscosity lines.

6.4 Results and Discussion

6.4.1 NMR Results

As shown in Figure 6.3, the ln(1/T1)−1/T slope does not change dramatically as temperature is cooled from room temperature into the hydrate region. This indicates the hydration cage structure around THF in the hydrate region before the phase transition is not very different from that at room temperature. The slope gives the average rotational activation energy of 21.18 kJ/Mole for THF in water solution, which is very different from that in the solid hydrate phase, 4.14 kJ/Mole.[109] Since the rotational activation energy reflects local water structure around THF, the result indicates that motion of THF in hydration shells in the aqueous phase is dissimilar in nature from motion in the regular clathrate cages in the hydrate phase, even under hydrate formation conditions. The suggested hydrate precursors were not found and the proposed hydrate formation hypothesis[1] is not supported.

To compare with the time dependent results reported by Oyama et al.[108], we measured T1 as a function of time while the temperature was kept constant under hydrate conditions. As shown in Figure 6.4, T1 doesn't change much with respect to
time during the induction period. This implies that the hydration shells around THF have no dramatic structural change and they do not rearrange themselves into regular clathrate cages during the induction time.

One interesting feature is that even though the slope of $\ln(1/T_1) - 1/T$ does not change dramatically as temperature goes from $\sim 25$ °C to hydrate formation regions, it does show a slight increase around 8–9 °C. In this experiment, the activation energy changes from 20 kJ/Mole to 24kJ/Mole at $\sim 8.5$ °C. This transition in the slope is very reproducible and it is under further investigation.

![Graph showing the relationship between $\ln(1/T_1/s)$ and $1/T/K$](image)

**Figure 6.3** $T_1$ of THF in liquid $D_2O$ before hydrate formation and after hydrate dissociation, plotted as $\ln(1/T_1/s)$ vs. $1/T/K$. The activation energies $E_a$s were calculated from the slopes.
Figure 6.4 $T_1$ of THF in D$_2$O during induction time at $-1.7^\circ$C.

After hydrate dissociation, even though the slope is similar to that before hydrate formation, there is a consistent shift of $T_1$ and it never returned to the original value. This variation of $T_1$ implies a structural change of water molecules around THF due to hydrate formation and dissociation. However, this structural change is not caused by residual clathrate structure because the effect still exists above 25 °C. There are possible microscopic heterogeneities$^{[110]}$ in fresh THF-D2O solution even though THF and D$_2$O are miscible at all concentrations under conditions of interest. Since THF becomes perfectly distributed as it forms hydrate, THF hydrate dissociation would result in a more microscopically homogenous THF-D2O solution. Therefore, the $T_1$ shift is probably caused by a more uniform distribution of THF in D$_2$O after THF hydrate dissociation than before hydrate formation. It was also observed that before hydrate formation the THF – D$_2$O solution had a slight milky appearance and after hydrate dissociation the solution became crystal clear. If without external disturbance, the milky appearance can last over two weeks at room temperature.
6.4.2 Viscosity Results

In the GC gas hydrate viscosity experiment, shown in Figure 6.5, the viscosity baseline after hydrate dissociation is obviously higher than that before hydrate formation at temperature 20 °C and pressure 1000 psi. The residual viscosity phenomenon reported in literature\(^{[88]}\) was successfully reproduced.

However, results from THF-water hydrate experiments (Figure 6.6) do not demonstrate a residual viscosity effect. Viscosities baselines established at 6 °C and 10 °C before hydrate formation are the same as those after hydrate dissociation. Macroscopic evidence of the residual structure is absent in this experiment. The different results from THF and GC experiments may be explained as follows.

![Graph showing ball travel time and temperature over elapsed time](image)

**Figure 6.5** Residual viscosity phenomenon was observed at 20 °C after Green Canyon gas hydrate dissociation with pressure kept constant at 1000 psi.
Figure 6.6 No residual viscosity is observed at 6 °C and 10 °C after THF hydrate.

In the GC hydrate experiment, after hydrate dissociation, large amounts of light hydrocarbons have to get out of the liquid phase because the concentrations of hydrocarbon gases in hydrate phases are much higher than their equilibrium concentrations in liquid water under the same condition. The hydrocarbon gases resulting from hydrate dissociation can come out of the liquid phase by diffusion or forming bubbles. Since the diffusion fluxes of hydrocarbons in water are very small, it is much more efficient for gases to escape in bubbles. However, from visual observation, few bubbles formed during GC hydrate dissociation under constant pressure. Therefore, gases come out of water mainly by diffusion, which will make this process very time consuming. During the time frame of viscosity measurements,
liquid water could be still highly supersaturated with hydrocarbon gases. This would cause higher than normal water apparent viscosity.\textsuperscript{111} THF doesn't have the above problem because its concentration in the liquid phase is the same as in the hydrate phase and it stays constant under all conditions. Since residual viscosity was absent about THF hydrate dissociation, the observed residual viscosity phenomenon in GC hydrate experiments was probably caused by supersaturated hydrocarbons in water after hydrate dissociation, not necessarily by any remaining clathrate structure in the aqueous phase.

The fact that residual viscosity was not observed after THF dissociation but an overall structural change around THF was indicated by NMR results may be explained by two reasons. First, strong mixing by the steel ball inside the sample tube may have already made THF-D\textsubscript{2}O microscopically homogenous even before hydrate formation and destroyed any residual structure as soon as hydrate melted. Second, even though CTHRC can reproduce the residual viscosity phenomenon for GC hydrate experiment, it may not be sensitive enough to detect the structural change after THF hydrate dissociation. In any case, the rocking cell type of apparatus\textsuperscript{88} may not be an appropriate tool to measure residual structure.

6.5 Conclusions

NMR and CTHRC techniques were used to investigate the formation and dissociation mechanisms of THF hydrate. In the NMR experiment, T\textsubscript{1} of THF in D\textsubscript{2}O was measured as the sample was cooled from room temperature into hydrate formation condition. By calculating the rotational activation energy of THF in D\textsubscript{2}O, it was shown that the THF hydration shell structure in solution doesn't change much
as temperature goes from room temperature to subzero. No indication of hydrate precursor formation was observed. During the induction period, $T_1$ stayed about the same as a function of time at constant temperature, which implied that water molecules in THF hydration shells don't undergo much rearrangement during the induction period. Results do not support the hydrate precursor hypothesis. After hydrate dissociation, $T_1$s were consistently smaller than that before hydrate formation, which suggests a fluid structural change after hydrate dissociation. However, this structural change is not evidence of residual clathrate structure because the effect did not disappear even at high temperatures. It is probably caused by a more uniform distribution of THF in D$_2$O after hydrate dissociation.

Using the CTHRC apparatus, a residual viscosity effect reported in literature was reproduced in GC gas hydrate experiments, but not in THF hydrate system. After GC gas hydrate dissociation under constant pressure, it would take a long time for hydrocarbon gases to reach their equilibrium concentrations because of their small diffusion constants in water. Combined with results from THF viscosity experiment, it is concluded that the residual viscosity phenomenon after GC gas hydrate dissociation is probably more due to gas supersaturation than residual clathrate structure. Since CTHRC did not manifest the fluid structural change after THF hydrate dissociation shown in the NMR experiments, rocking cell type of apparatus may not be an effective technique to study residual clathrate structure.
Chapter 7. NMR/MRI Study of Clathrate Hydrate Mechanisms

7.1 Summary

Clathrate hydrates are of great importance in many aspects. However, hydrate formation and dissociation mechanisms, essential to all hydrate applications, are still not well understood due to the limitations of experimental techniques capable of providing dynamic and structural information on a molecular level. NMR has been shown to be a powerful tool to non-invasively measure molecular level dynamic information. In this work, we measured Nuclear Magnetic Resonance (NMR) Spin Lattice Relaxation Times ($T_1$) of tetrahydrofuran (THF) in liquid deuterium oxide ($D_2O$) during THF hydrate formation and dissociation. At the same time, we also used Magnetic Resonance Imaging (MRI) to monitor hydrate formation and dissociation patterns. Results showed solid hydrate significantly influences coexisting fluid structure. Molecular evidence of residual structure was identified. Hydrate formation and dissociation mechanisms were proposed based on the NMR/MRI observations.

7.2 Introduction

Gas hydrates are ice-like structures in which water molecules, under pressure, form structures composed of polyhedral cages surrounding gas molecule "guests" such as methane and ethane. Rarely encountered in everyday life, they occur in staggering abundance under sea floor and permafrost environments where (P, T) conditions ensure their stability. The natural gas trapped in these deposits represents a potential source of energy many times all known natural gas reserves.

Hydrates can form as well in undersea piping and above ground gas pipelines where they pose a major problem for gas/oil producers.

Detailed understanding of hydrate melting and formation mechanisms on a molecular level is important for successfully tackling all hydrate challenges with accuracy and confidence. However, hydrate growth and dissociation mechanisms still remain unclear because very few experimental techniques can provide in situ dynamic information on a molecular scale. Liquid water structure coexisting with the hydrate phase, especially near the water/hydrate interface, is very important in understanding the hydrate formation and dissociation processes. The imminent state before guest molecules solidify into the hydrate phase and the fluid structure immediately after clathrate hydrate dissolves into the liquid state may hold the key to unlock the secrets of hydrate mechanisms.

NMR has been shown to be a powerful tool to non-invasively measure molecular level dynamic information. $T_1$ is an indicator of local molecular order around the spin bearing molecules. $T_1$ measurement is an effective method to monitor microscopic fluid structure change. In this work, NMR $T_1$ measurements of THF in D$_2$O solution were employed to probe the change of water structure around THF during THF hydrate formation and dissociation to understand the role of the water and hydrate interface. Proton MRI was also utilized to observe the hydrate formation and dissociation patterns.

THF molecules become invisible to liquid state NMR spectroscopy as they are incorporated into the solid hydrate phase; thus, $T_1$ of THF in the liquid phase can be measured independently of the THF hydrate. D$_2$O is invisible to proton NMR
under all conditions, so only THF in the liquid phase is visible to MRI. Results showed solid hydrate presence significantly influences the fluid structure. \( T_1 \) measurements also indicated the existence of residual effects after hydrate dissociation.

7.3 Experimental Details

The schematic of the experimental setup is shown in Figure 7.1. \( T_1 \) measurements of THF (Aldrich, 99+% in \( D_2O \) (Cambridge Isotope Laboratories, \( D \) 99.9%) and MRI imaging experiments were performed on an 85 MHz Oxford horizontal 32 cm wide bore NMR with imaging capability, using a LITZ RF Volume Coil (with 14 cm internal diameter) from Doty Scientific, Inc. Data were acquired and processed using Varian VNMR software and INOVA hardware systems. \( T_1 \)s were measured using inversion and recovery technique. VNMR software, given inputs of possible minimum and maximum \( T_1 \) values, automatically generates standard 180°-\( \tau \)-90° pulse sequences with various values of delay time \( \tau \). It took 4~6 minutes to take a \( T_1 \) data point and about one hour to take a MRI image.

Figure 7.1 Experimental schematic.
An Air-Jet temperature controller supplied dry and cold air to control the sample temperature. It is capable of controlling temperature from \(-40^\circ C\) to \(100^\circ C\) with \(0.1^\circ C\) stability. A glass bottle with a cap that has a Teflon® liner was used to contain 29 ml of THF-D$_2$O solution (molar ratio 1:17) and was tightly sealed to prevent THF evaporating into the environment. The sample was weighed and no THF loss was detected after a long period of time. A LUXTRON® fluoroptic thermometer was mounted into the glass container through the cap to monitor the sample temperature. Its output reading resolution is \(0.1^\circ C\).

Since trace amounts of oxygen may alter T$_1$ of THF significantly, pure D$_2$O and THF liquids were deoxygenated separately in a closed glove box with nitrogen environment. D$_2$O and THF were contained in two separate Teflon bottles. The gas phase above the liquid phase was periodically flushed with nitrogen gas and the bottles were periodically shaken to facilitate the diffusion of oxygen out of the liquid phase. After the gas phase had been flushed six or seven times over about 12 hours, THF and D$_2$O were mixed on the molar basis of 1:17 in the glass bottle. This is the same concentration of THF in D$_2$O in the hydrate phase. Therefore, as hydrate is formed, the liquid phase composition will not change. The sample was then sealed and moved into the probe for T$_1$ measurements. (The success of deoxygenation was demonstrated by that fact that after deoxygenation, T$_1$ of THF in liquid D$_2$O increased about 2 seconds compared to the sample without deoxygenation).

In a recent paper,\textsuperscript{113} we reported that T$_1$ of THF in D$_2$O after THF hydrate dissociation is consistently smaller than that before hydrate formation. It was
suggested that the change in $T_1$ is due to the THF-D$_2$O solution becoming more microscopically homogenous after hydrate dissociation than before hydrate formation. To investigate residual clathrate hydrate structure after hydrate dissociation by $T_1$ measurements, it is important to ensure that the THF-D$_2$O solution is already homogenous and in its equilibrium configuration before hydrate formation. Then if the $T_1$ after hydrate dissociation is different from that before hydrate formation, it would be strong evidence of residual clathrate hydrate structure. Therefore, in this study, the freshly mixed THF-D$_2$O solution was first turned into hydrate and subsequently dissociated, in order to make the sample solution microscopically homogeneous before $T_1$ and MRI measurements. To eliminate any possible residual clathrate structure, the THF-D$_2$O solution was heated to 35 °C after hydrate dissociation and equilibrated at room temperature for 24 hours. $T_1$ measurement was then started as the sample was cooled down in steps until hydrate nucleation, which was indicated by a sudden rise of the sample temperature. The temperature of the cooling air was then adjusted to slow the hydrate formation rate for better $T_1$ measurement and imaging experiments. After complete hydrate formation, marked by the disappearance of THF peaks in the NMR spectrum, the temperature was raised to slowly dissociate the hydrate. Right after complete hydrate dissociation, the temperature was cooled down to form hydrate again, in order to examine the memory effect. After the reformation was complete, THF was dissociated and the temperature was raised to room temperature in steps. Images of hydrate formation and dissociation patterns were taken by MRI technique using Spin Echo Multi Slice (SEMS) pulse sequence. The parameters were adjusted to produce
proton density weighted images, which depend primarily on the density of protons in the imaging volume with the effects of $T_1$ and $T_2$ minimized. The orientation of the image slice was in the horizontal direction.

![Graph](image)

**Figure 7.2** $T_1$ behavior of THF at various temperatures and conditions.

### 7.4 Results and Discussion

The dependence of $\ln(1/T_1)$ on $1/T$ ($T$ is temperature in K) during cooling, hydrate formation, hydrate dissociation, and warming up, is plotted in Figure 7.2. The relationship is linear during cooling and warming up. Every $T_1$ data point was measured with a standard deviation less than 0.05s. It required substantial subcooling to initiate hydrate formation. The reported slope change around 8 to 9 °C
during cooling was reproduced.\textsuperscript{[113]} The free induction decay and sign of the slope indicate the motion of THF in D\textsubscript{2}O solution is in the extreme narrowing region, i.e., the rotational correlation time of THF $\tau_c$ is less than $10^{-9}$ s. Based on NMR theory,\textsuperscript{[107]} the rotational activation energy of THF, $E_a$, can be calculated from the slope if the relation $\tau_c = \tau_c \exp\left(E_a / RT\right)$ is assumed, where $R$ is the universal gas constant. The resulting $E_a$s for the cooling and warming up processes in the temperature range 8 – 25 °C are the same, 18 kJ/mol. There still is a slight shift in $T_1$ after hydrate dissociation compared to before hydrate formation. However, the difference is minuscule compared to the $T_1$ change after dissociating the hydrate that formed from fresh THF-D\textsubscript{2}O solution\textsuperscript{4}. It is probably because in this experiment THF was already homogenously distributed before hydrate formation and its distribution did not change much after hydrate dissociation.

One interesting feature in Figure 7.2 is that $T_1$ values of THF in the liquid phase during hydrate formation and dissociation fall far off the linear lines for the cooling and heating processes in the single liquid phase. Since the concentration of THF in the liquid phase remains unchanged during hydrate formation/dissociation, it reveals that the presence of solid hydrate strongly influences its coexisting fluid structure. The liquid / hydrate interface probably plays an important role through the O-H bonds of the partial cages on the hydrate surface sticking into and structuring the liquid phase. Figure 7.3 shows the change of $T_1$ as a function of peak height, i.e., the amount of remaining liquid, during hydrate formation and dissociation. As the amount of liquid diminishes and more hydrate is present, $T_1$ of THF gets higher. One possibility is a higher percentage of the water being structured by the hydrate
surface, as more hydrate is present. This structured interface hypothesis is in agreement with the "reaction film" proposition by Clarke and Bishnoi\textsuperscript{[114]} for hydrate growth. Figure 7.3 also reveals that $T_1$s during hydrate dissociation are higher than those during hydrate formation under the same conditions and phase composition. This difference in $T_1$ between formation and dissociation transitions indicates a difference in fluid structure. This difference can be argued as the evidence of residual hydrate structure. However, this residual structure does not necessarily mean clathrate aggregates remaining in solution.\textsuperscript{[115]} It could be residual hydrogen bonds from collapsing of the solid clathrate structures. After complete hydrate dissociation, $T_1$ returned to normal values within 16 hours without further raising the temperature.

![Graph showing $T_1$ as a function of NMR peak height](image)

**Figure 7.3** $T_1$ as a function of NMR peak height, i.e., the amount of liquid, during hydrate formation and dissociation.

MRI images of hydrate formation and dissociation patterns were also taken for better understanding of hydrate growth and dissociation mechanisms. A higher degree of subcooling and a longer induction time were required to form THF hydrate
for the first time. Once hydrate started to form, formation was rapid because the sample temperature was lower than the equilibrium temperature. MRI images of hydrate formation are shown in Figure 7.4. It was demonstrated that hydrate nucleated homogenously along the perimeter of the sample and formed from the outside inward.

![Images showing hydrate formation](image)

**Figure 7.4** THF hydrate formation pattern from THF- D$_2$O solution. White area is the liquid phase. THF hydrate is invisible to MRI.

After hydrate formation was complete, the temperature was raised to melt the hydrate. As shown in Figure 7.5, hydrate started to melt along the perimeter. The dissociation progressed along the hydrate/liquid interface toward complete dissociation, which was indicated by the NMR peak heights returning to the original values before hydrate formation. To examine the memory effect and hydrate reformation pattern, the sample was cooled down to form hydrate again right after the dissociation was complete. This time it required shorter induction time and less
subcooling. The hydrate formation was also gradual compared to last time. The formation kinetics could be well controlled by changing the cooling air temperature.

![Figure 7.5 Hydrate dissociation pattern as the sample is warmed from the perimeter.](image)

Figure 7.5 Hydrate dissociation pattern as the sample is warmed from the perimeter.

The MRI images of hydrate reformation were displayed in Figure 7.6. The nucleation took place at a point near the wall of the sample bottle instead of homogenously along the sample perimeter as it formed hydrate for the first time. It may be due to a hydrate residual structure mentioned earlier, which functioned as a nucleation seed. Both $T_1$ and MRI experiments were repeated several times to confirm their reproducibility.

![Figure 7.6 Reformation pattern of THF hydrate from THF-D$_2$O solution that formed hydrate before. Hydrate formation progresses from (a) to (c).](image)
In summary, $T_1$ measurements of THF in the liquid phase during hydrate formation and dissociation strongly suggest that presence of solid hydrate coexisting with the liquid phase influences the fluid structure, probably through hydrogen bonding between the liquid and the solid at the interface which creates a structured liquid layer. As expected, MRI images showed that once hydrate nucleates, hydrate grows only at the hydrate / water interface, even though the THF concentration is homogenous in the liquid phase. Hydrate only dissociates at the interface even though the temperature is uniform in the solid hydrate. Tohidi et al.$^{[115]}$ discovered that hydrates isolated from the liquid phase require higher than equilibrium temperature to dissociate, which demonstrated the important role of the liquid-hydrate interface for hydrate dissociation. Ikeda-Fukazawa and Kawamura$^{[116]}$ simulated ice melting using molecular dynamics. It was concluded that the dangling motion of the free O-H bonds on the ice surface is the main cause of destructing ice crystal structure.

The above observations lead to the following hypothesis about hydrate mechanism. The structured liquid water at the hydrate surface is the key to hydrate growth and dissociation. During hydrate growth, water and THF molecules near the hydrate surface are structured into a semi-clathrate organization while the water network away from the interface is still in the normal liquid state. This structured liquid layer causes hydrate to preferentially form at the interface instead of elsewhere and it facilitates hydrate growth. During hydrate dissociation, kinetic energy is transmitted through the motions of the hydrogen bonds in the structured layer to break down the solid clathrate structure.
7.5 Conclusions

$T_1$ measurements and MRI techniques were employed to investigate THF hydrate formation and dissociation to improve the understanding of clathrate hydrate mechanisms. It was found that the simultaneous presence of water and hydrate significantly increases the $T_1$ of THF in the coexisting liquid phase – the more the hydrate, the higher the $T_1$. This is probably because the lower the liquid fraction, the greater structuring of the coexisting liquid phase, which causes $T_1$ to increase further. MRI images demonstrated that hydrate grows and dissociates along the hydrate/water interface. Combined with results from $T_1$ measurements, it was proposed that the structured water layer in contact with the hydrate surface is the key to both hydrate growth and dissociation. The structured layer causes hydrate to preferentially form at the hydrate/water interface and facilitates hydrate growth. During hydrate dissociation, the kinetic energy of liquid water is transferred through the structured layer to collapse the hydrogen-bonding network in the solid hydrate.

Reformation of THF hydrate right after hydrate dissociation required less subcooling and shorter induction time than the initial hydrate formation. This memory effect is probably due to the existence of residual structures in the hydrate melt, which is supported by the higher $T_1$ of THF during hydrate dissociation than during hydrate formation.
Chapter 8. Application of Low Field NMR $T_2$ Distribution to Clathrate Hydrates

8.1 Summary

Low field Nuclear Magnetic Resonance (NMR) spin-spin relaxation time ($T_2$) distributions were employed to investigate tetrahydrofuran (THF) clathrate hydrate formation and dissociation in deuterium oxide ($D_2O$). Because the $T_2$'s of THF molecules reflect the dynamics of the surrounding water structure, $T_2$ distributions yield microscopic insights into the hydrate formation and dissociation processes. It was found that such $T_2$ measurements could easily distinguish THF in a solid hydrate phase from THF in the coexisting liquid phase. This is the first time that $T_2$ of guest molecules in hydrate cages has been measured using this technique. It was also shown that $T_2$ of THF in the liquid phase changes as hydrate formation/dissociation progresses, implying that the presence of solid hydrate influences the coexisting fluid structure.

8.2 Introduction

Gas hydrates, also known as clathrate hydrates, are ice-like compounds in which water molecules, under high pressures and low temperatures, form structures composed of nano-scale polyhedral cages that surround small guest molecules such as methane and ethane.\(^1\) The importance of gas hydrates has been realized in many areas, including flow assurance,\(^2\) global climate models,\(^5\) and potential future energy resources.\(^3\) However, knowledge of the molecular mechanisms of hydrate formation/dissociation and intrinsic hydrate kinetics is still relatively limited. Understanding at this fundamental level has been hindered mainly by the lack of
experimental tools that are capable of directly observing the hydrate phase and sensitive enough to detect rapid molecular motions and environments.

NMR T\textsubscript{2} distributions have been routinely applied in the petroleum industry to characterize rock matrix and measure downhole fluid\textsuperscript{[117]} This technique has rarely been used to investigate gas hydrates. An attempt by Schlumberger\textsuperscript{[118]} to measure T\textsubscript{2} distributions in methane hydrate using a 2MHz Resonance Instruments (RI) Maran spectrometer failed in obtaining methane T\textsubscript{2} data in hydrate cages, probably because the free induction decay signal of the methane in hydrate is shorter than the dead time of the instrument. Garg et al.\textsuperscript{[119]} reported the proton line widths of THF in D\textsubscript{2}O hydrate at various temperatures, measured by wide-line spectroscopy at 16 MHz. Assuming Gaussian lineshapes, this data would indicate T\textsubscript{2}'s of about 0.5 ms for THF at 207K, which should be long enough to be measurable by a 2MHz RI Maran spectrometer that has probe dead time of 60 \textmu s. Since T\textsubscript{2} is an indicator of the local molecular ordering around the spin-bearing molecules, the T\textsubscript{2} distributions of THF in D\textsubscript{2}O during hydrate transitions should provide a new way of gathering information regarding hydrate molecular mechanisms.

In this work, NMR T\textsubscript{2} distribution measurements were used to monitor THF/D\textsubscript{2}O hydrate formation and dissociation processes. Results demonstrated that the T\textsubscript{2} distribution of THF molecules in D\textsubscript{2}O clathrate cages can be fully captured with a 2MHz RI Maran coincidently with the T\textsubscript{2} distribution of THF molecules from within a coexisting liquid phase. To our knowledge, this is the first time T\textsubscript{2} of the guest molecules in hydrate cages has been measured using the NMR T\textsubscript{2} distribution technique. The influence of hydrate phase on the coexisting fluid structure\textsuperscript{[120]} was
also suggested by the change of $T_2$ of THF in the liquid phase as the solid to liquid ratio changes at hydrate equilibrium temperature. Since the area under the $T_2$ distribution of the hydrate phase represents the population of the enclathrated THF, extension of this technique can provide information on intrinsic hydrate kinetics.

### 8.3 Experimental Details

The schematic of the experimental setup is shown in Figure 8.1. $T_2$ distribution measurements of the protons in THF (Aldrich, 99+%) in D$_2$O (Cambridge Isotope Laboratories, D 99.9%) were obtained with a 2 MHz RI Maran NMR spectrometer using Carr-Purcell-Meiboom-Gill (CPMG) technique. This instrument has a probe dead time of 60 μs. In the CPMG pulse sequence, the 90-180 degree pulse gap is 166.7 μs. Data were acquired by RiNMR software and processed using WinDXP program.

![Figure 8.1 Experimental schematic.](image)

The temperature of the spectrometer has to be kept constant at 30 °C to maintain stability of the system's permanent magnet. Therefore, thermal insulation material was placed along the inside surface of the sample bore as an Air-Jet
temperature controller supplied dry air to control the sample temperature. This controller is capable of providing air temperature from $-40 \, ^\circ C$ to $100 \, ^\circ C$ with $0.1 \, ^\circ C$ stability. A glass bottle with a cap that has a Teflon liner was used to contain 20 ml of THF-D$_2$O solution (molar ratio 1:17) and was tightly sealed to prevent THF evaporating into the environment. The sample was weighed and no THF loss was detected after two weeks. A LUXTRON fluoroptic thermometer was mounted into the glass container through the cap to monitor the sample temperature with a resolution of $0.1 \, ^\circ C$.

Since trace amounts of oxygen may alter $T_2$ of THF significantly, pure D$_2$O and THF liquids were deoxygenated separately in a closed glove box with nitrogen environment. D$_2$O and THF were contained in two separate Teflon bottles. The gas phase above the liquid phase was periodically flushed with nitrogen gas and the bottles were periodically shaken to facilitate the diffusion of oxygen out of the liquid phase. After the gas phase had been flushed six or seven times for about 12 hours, THF and D$_2$O were mixed on the molar basis of 1:17 in the glass bottle. This is the same concentration of THF as in the hydrate phase. Therefore, as hydrate forms, the liquid phase composition should not change. The sample was then sealed and moved into the Maran for measurements. It was carefully placed in the "sweet spot" of the magnet, the spot where the magnetic field is the most homogenous.

In a recent paper,$^{[113]}$ we reported that the proton spin lattice relaxation time ($T_1$) of THF in D$_2$O after THF hydrate dissociation is consistently smaller than that before hydrate formation. It was suggested that the change in $T_1$ is due to the THF-D$_2$O solution becoming more microscopically homogenous after hydrate dissociation
than before hydrate formation. To ensure that the THF-D$_2$O solution is already homogenous and in its equilibrium configuration before hydrate formation, in this study, the freshly mixed THF-D$_2$O solution was first turned into hydrate and subsequently dissociated. It was warmed up to 35 °C for about two hours to eliminate any possible remnant hydrogen bonding structure.\textsuperscript{10} $T_2$ measurements were started as the sample was cooled down in steps until the point of hydrate nucleation, which is identified by the sudden rise of the sample temperature. The temperature of the cooling air was then adjusted to slow the hydrate formation rate for better $T_2$ measurements. After each measurement, \textit{WinDXP} program was run to calculate the $T_2$ distribution. It took about 5 – 10 minutes to complete a single measurement, depending on the number of scans and the delay time between two consecutive scans. The relaxation delay time should be longer than 5$T_1$ to allow the spins to fully recover before next excitation. After complete hydrate formation, marked by the disappearance of the THF liquid peak in the $T_2$ distribution, the sample was further cooled down to measure the $T_2$ behavior of THF in THF hydrate with regard to temperature. Then the sample was warmed up to slowly dissociate the hydrate and the temperature was subsequently raised to room temperature in steps.

\textbf{8.4 Results and Discussion}

$T_2$ distributions of THF in D$_2$O during hydrate formation are presented in Figure 8.2, along with the $T_2$ distribution before hydrate formation at 7.5 °C, which is close to the THF/D$_2$O hydrate equilibrium temperature ~7.4 °C that was measured in this work. It is evident that THF in the hydrate phase and the coexisting liquid phase
can be easily distinguished as two nicely separated peaks. The $T_2$ of THF in hydrate phase is $\sim 2 - 3$ ms, while the $T_2$ of THF in liquid phase changes from 4.2 s to 3.5 s to 2 s as the percentage of hydrate in the sample increases from 0% to 55% to 90%. As shown in Figure 8.3, during hydrate formation, the hydrate peak area increases while the liquid peak area decreases, and the sum of hydrate and liquid peak areas is conserved with $\sim 5\%$. The conservation of total peak area adds confidence to the assumption that during the transition THF molecules inhabit two distinct states. Lines were added to guide the eyes.

![Figure 8.2](image)

**Figure 8.2** $T_2$ distributions of THF in D$_2$O at different hydrate conversion percentages during hydrate formation, compared with the $T_2$ distribution of THF in D$_2$O before hydrate formation at the hydrate equilibrium temperature.
Figure 8.3 Peak areas of THF in liquid phase and hydrate phase during hydrate formation as a function of time. Lines were added to guide the eyes.

Figure 8.4 $T_2$ behaviors of THF in D$_2$O solution at different temperatures and conditions.

The dependence of $\ln(1/T_2)$ on $1/T$ (T is temperature in K) during cooling, hydrate formation, hydrate dissociation, and warming up, is plotted in Figure 8.4. The error of each data point is less than 6.14%, based on the time scale resolution.
According to NMR theory\textsuperscript{11}, the rotational activation energy of THF, $E_a$, a measure of local molecular ordering around the NMR responding molecules, can be calculated from the slope of $\ln(1/T_2) \sim 1/T$ if the rotational motion is in the extreme narrowing region and the Arrhenius equation $\tau_c = \tau_0 \exp(E_a / RT)$ is assumed. In this equation, $R$ is the universal gas constant; $\tau_c$ - reorientational correlation time; $\tau_0$ - time constant at infinite temperature. The relationship during cooling can be fitted to two linear regions with each R-squared value better than 0.99. This previously observed slope deviation\textsuperscript{113} during the cooling process, located 1~2 °C above the hydrate equilibrium temperature, suggests a change in the molecular motion of THF in the liquid phase as temperature decreases. The detailed mechanism is still to be understood. Difference was noticed between heating and cooling processes, but it is within experimental uncertainty. A line was added to guide the eyes for data during warming up.

Our earlier work\textsuperscript{120} reported that $T_1$ (85 MHz) of liquid THF in D$_2$O during hydrate transition varies as hydrate formation or dissociation progresses. This implies the fluid structure during hydrate transition is different from the fluid structure in which hydrate is not present. $T_2$ (2 MHz) results from this work also changed with the progress of hydrate transition at constant temperature. Figure 8.5 presents the $T_2$ of THF in D$_2$O solution as a function of the liquid phase fraction during hydrate transition – the less the liquid, the shorter the $T_2$. This observation supports the proposition that the presence of a hydrate phase influences the hydrogen bonding network of the coexisting liquid phase. Hydrate transition was held at certain solid-to-liquid ratios for overnight. No $T_2$ change with time was observed, which suggests this
hydrate influence on the liquid structure is not transient but stable. A slight difference in \( T_2 \) was observed between hydrate formation and dissociation (Figure 8.5).

**Figure 8.5** \( T_2 \) of THF in D\(_2\)O solution as a function of the liquid phase fraction during hydrate formation and dissociation.

\[ T_2(s) \]

\[
\begin{array}{c|c|c|c|c|c}
\text{Fraction of the Liquid Phase, %} & 0 & 20 & 40 & 60 & 80 & 100 \\
\hline
T_2 (s) & 3.9 & 3.5 & 3.1 & 2.7 & 2.3 & 1.9 \\
\end{array}
\]

**Figure 8.6** \( T_2 \) of THF in D\(_2\)O clathrate cages in the temperature range of 260K – 275K, plotted as ln(1/T\(_2\)/ms) vs. 1/T/K.

\[ \text{E}_a = 31\text{KJ/Mole} \]

\[ \text{ln}(1/\text{T}_2/\text{ms}) \]

\[
\begin{array}{c|c|c|c|c|c}
1/T/K & 0.00357 & 0.00364 & 0.00371 & 0.00378 & 0.00385 \\
\hline
\text{ln}(1/\text{T}_2/\text{ms}) & -0.4 & -0.6 & -0.8 & -1.0 & -1.2 \\
\end{array}
\]

\( T_2 \)'s of THF in hydrate phase were measured in the temperature range of ~260K – 275K, plotted as ln(1/T\(_2\)/ms) ~ 1/T/K in Figure 8.6. Combined with the
Arrhenius equation $\tau_c = \tau_0 \exp\left(\frac{E_a}{RT}\right)$, the slope of $\ln(1/T_2/\text{ms}) \sim 1/T/K$ gives the motional activation energy of THF in D$_2$O clathrate cages, 31KJ/Mole. Considering that the temperature range in this work is limited, this value fortuitously agrees with the activation energy given by Garg$^7$, ~30KJ/Mole, and the value given by Hayward and Packer$^{12}$, 33KJ/Mole. As suggested by Hayward and Packer, this high activation energy is probably due the breaking of a hydrogen bond.

8.5 Conclusions

For the first time, $T_2$ of THF in D$_2$O clathrate cages was obtained using low field NMR $T_2$ distribution measurement, giving a mean value about 2ms. It was demonstrated that the $T_2$ distribution technique is a valuable tool for investigating clathrate hydrate mechanisms, capable of obtaining dynamic molecular information of both hydrate phase and the coexisting liquid phase simultaneously during hydrate transition. Due to its ability of directly measuring the extent of hydrate conversion in a timely manner, extension of this technique can be potentially applied to gather hydrate kinetic data.

As temperature decreases from higher to lower regions, a slope change of $\ln(1/T_2) \sim 1/T$ was observed, indicating the motion of THF molecules undergoes certain transformation. $T_2$ of THF in D$_2$O solution decreases as hydrate formation progresses, suggesting the fluid structure changes as more hydrate is present. A slight difference in $T_2$ was observed between hydrate formation and dissociation. The activation energy for the rotation of THF in hydrate phase was calculated to be 31KJ/Mole in the temperature range 260K – 275K.
Chapter 9. Detecting Gas Hydrate Behavior in Crude Oil Using NMR

9.1 Summary

Because of the associated experimental difficulties, natural gas hydrate behavior in black oil is poorly understood despite its grave importance in deep-water flow assurance. Since the hydrate cannot be visually observed in black oil, traditional methods often rely on gas pressure changes to monitor hydrate formation and dissociation. Because gases have to diffuse through the liquid phase for hydrate behavior to create pressure responses, the complication of gas mass transfer is involved and hydrate behavior is only indirectly observed. This pressure monitoring technique encounters difficulties when the oil phase is too viscous, the amount of water is too small, or the gas phase is absent.

In this work we employ proton Nuclear Magnetic Resonance (NMR) spectroscopy to observe directly the liquid-to-solid conversion of the water component in black oil emulsions. The technique relies on two facts. The first, well known, is that water becomes essentially invisible to liquid state NMR as it becomes immobile, as in hydrate or ice formation. The second, our recent finding, is that in high magnetic fields of sufficient homogeneity, it is possible to distinguish water from black oil spectrally by their chemical shifts. By following changes in the area of the water peak, the process of hydrate conversion can be measured, and, at lower temperatures, the formation of ice. Taking only seconds to accomplish, this measurement is nearly direct in contrast to conventional techniques that measure the pressure changes of the whole system and assume these changes represent formation or dissociation of hydrates – rather than simply changes in solubility. This
new technique clearly can provide accurate hydrate thermodynamic data in black oils. Because the technique measures the total mobile water with rapidity, extensions should prove valuable in studying the dynamics of phase transitions in emulsions.

9.2 Introduction

When natural gases come into contact with water under high pressures and low temperatures, they form ice-like crystalline compounds called gas hydrates, which are composed of nano-scale water cages that enclose gas molecules of appropriate diameters.\textsuperscript{[1]} Hammerschmidt\textsuperscript{[14]} first realized it was gas hydrates, not ice, that were plugging natural gas pipelines. This marked the beginning of the industrial interest in gas hydrates for flow assurance, i.e., assurance of unrestricted flow of fluids through pipelines. Due to the frequent presence of water and light hydrocarbons, like methane, during oil production, hydrate plug formation is a serious concern in deep-water flow-assurance of oil and gas flow lines, where high pressures and low temperatures are often encountered. To prevent hydrate plugging, appropriate amounts of chemical hydrate inhibitors are often added into the pipelines or thermal insulations are installed to prevent heat loss. It was estimated that industry is spending over 500 million dollars on hydrate inhibitors annually.\textsuperscript{[12]}\textsuperscript{[1]} The dose rates of hydrate inhibitors and thermal insulation designs are all based on the expected pipeline conditions relative to the hydrate phase diagram.\textsuperscript{[8]} Therefore, accurate phase diagrams of gas hydrates are essential to safety and economic considerations. Equally important is hydrate formation and dissociation kinetics, a key factor in hydrate management. Unfortunately, current models for predicting
hydrate phase behavior show considerable discrepancy with experimental data for black oil systems.\cite{9} The differences can be as much as 5-6 degrees,\cite{9} which will either invoke unnecessary expense or put the operation at great risk. New, accurate experimental data is needed to test and tune phase behavior models.\cite{9} However, hydrate phase behavior in black oil, particularly with emulsions, is poorly understood due to the associated experimental difficulties. No kinetic data on gas hydrates in black oil has been reported in the literature.

In multi-hydrate-former systems like natural gas and black oil, the hydrate thermodynamic point is defined as the equilibrium condition at which the last hydrate crystal dissociates.\cite{96} Because the nature of black oil deters direct visual observation, traditional attempts to characterize hydrate behavior in black oil have frequently depended on monitoring system pressure changes.\cite{6} In this method, water, black oil, and gas are charged into a high-pressure cell. The pressure is monitored as this closed system is ramped in temperature. Because the gases have to transport through the liquid oil and water phase, some means of mechanical stirring are often employed to facilitate the gas mass transfer. Pressure drops dramatically upon hydrate formation because hydrate formation consumes large quantity of gas. After hydrate formation, the temperature is raised to dissociate the hydrate. As hydrate dissociates, gases are released and pressure increases significantly. The transition point that indicates complete hydrate dissociation, (normally where pressure and temperature return to the original P, T curve before hydrate formation), is identified as the hydrate thermodynamic point.
This traditional pressure-temperature monitoring technique is widely used, but has some inherent limitations. For example, it can be troublesome in obtaining accurate hydrate thermodynamics and kinetics when the oil phase is too viscous. Because gas diffusion rates in the oil are small, a long delay between hydrate behavior and pressure response is to be expected\textsuperscript{6}. Because the dissociation of a small hydrate crystal in black oil is not likely to cause much pressure change, it is very challenging to locate accurately the hydrate thermodynamic equilibrium point. The traditional technique also has difficulties in very low water-cuts. If the amount of water is too small, hydrate formation may not cause enough pressure change for accurate hydrate point measurements. Further complications arise when the pressure is above the oil bubble point where the gas phase disappears.

To overcome these limitations, in this work, we demonstrate the viability of employing proton Nuclear Magnetic Resonance (NMR) spectroscopy to directly and accurately observe in situ hydrate behavior in black oil. In a proton NMR spectrum, different hydrogen functional groups have different chemical shifts, as shown in Figure 9.1.\textsuperscript{100} The chemical shifts of water and saturated hydrocarbons, the dominant component in the black oil and natural gas, are about 3ppm apart.\textsuperscript{100} Thus, the water and oil components should be distinguishable in a high field NMR with sufficient magnetic field homogeneity. The water peak area in the NMR spectrum is directly related to the amount of liquid water in the sample. Because the free induction decay of water in gas hydrates at these fields is so short, and their spectral line so broad, they cease to contribute to the liquid water peak, and consequently the water peak decreases. We can immediately detect and easily
quantify hydrate formation and dissociation from the changes of water peak area, instead of depending on pressure responses like in the traditional method. Using this method, we can dynamically and accurately measure when hydrates nucleate or dissociate, their concentration in the system, and how fast hydrates are forming or dissociating, and therefore obtain accurate hydrate thermodynamic and kinetic information in black oil.

![Diagram](image)

**Figure 9.1** Proton NMR chemical shifts for common functional groups.

### 9.3 Experimental Details

The experimental scheme is depicted in Figure 9.2. The magnet for NMR measurements is an 85 MHz Oxford horizontal 32cm wide bore NMR with imaging capability. The probe is a LITZ RF Volume Coil (with 14 cm internal diameter) from Doty Scientific, Inc. NMR data were acquired and processed using Varian VNMR software and INOVA hardware systems.
To mimic the situation during oil production, black oil and pure water were mixed in a 1:1 volume ratio and manually shaken to make a stable water-in-oil emulsion. Baker Petrolite generously provided the black oil samples. The pure water was from Aldrich Chemical Company Inc. and used without further processing. The 16 ml water-in-oil emulsion sample was contained in a Teflon® bottle and then placed in a core holder from Temco Inc, which is made of strong non-metal composite material and specially designed for NMR experiments. The core holder is capable of handling pressures up to 2500 psi. It has an outer diameter of 5.6cm, inclosing the sample itself of 2.7cm diameter and 3.1cm height. Ultra High Purity (UHP) grade methane from Airgas was used as the gas phase. A Ruska positive displacement hand-pump controlled the pressure. Its maximum pressure capability is 4000 psi. The gas pressure was accurately measured by a Heise high precision dial pressure gauge with 2.5 psi resolution.
An Air-Jet temperature controller blew dry air to control the core holder temperature. It is capable of controlling temperature from −40°C to 100°C with ±0.1°C stability. Styrofoam material was placed around the core holder for insulation. A LUXTRON® fluoroptic thermometer with resolution of 0.1°C was mounted onto the core holder to monitor the temperature. Temperature of the core holder itself was measured at the same axial location of the sample (a radial distance of 2.8cm). The temperature difference between sample volume and core surface was measured in a separate measurement at room pressure after a 5°C step and found to be less than 0.1°C after 2 hours of equilibration. During hydrate measurements (at 2000 psi density methane) temperature gradient should be less.

With the emulsion sample inside and insulation outside, the core holder was placed into the NMR probe. Magnetic Resonance Imaging (MRI) techniques were utilized to ensure the sample was located in the center of the magnet, the spot that has the most homogenous magnetic field. The more homogenous the magnetic field, the better are the spectral resolution and signal to noise ratio. The core holder was then slowly pressurized to 2000 psi with methane at room temperature. The system was allowed to stabilize at room temperature and 2000 psi for one day to allow as much as gas as possible to dissolve into the oil/water phases. Over this period the consumption of gas required to maintain the pressure diminished to zero. The NMR system was fine-tuned to yield a spectrum in which the water peak was easily distinguishable from oil/gas peaks.

After the pressure was stabilized, indicating the system had reached equilibrium, the temperature control was turned on to slowly cool down the core
holder in steps. To ensure maximum hydrate formation before the sample went into
the subzero region where ice may form, the system was held at ~0°C for two weeks.
The temperature was then further cooled down to the extent where most of the water
peak disappeared. After the disappearance of the water peak, the core holder was
heated up in steps to dissociate the solid phases. Under all conditions, the pressure
was kept constant at 2000 psi through the Ruska hand-pump. The temperature was
held constant at each step for over 12 hours before each measurement. NMR
spectrum was collected at every temperature step to detect any change in water
peak area, i.e. the indication of hydrate formation or dissociation in black oil.

![NMR spectra](image)

**Figure 9.3** NMR spectra at different stages of the experiment. From (a) to (d),
as less mobile water is present, the water peak diminishes.

### 9.4 Results and Discussion

Figure 9.3 shows the NMR spectra of the water/black oil emulsion sample
with different degrees of hydrate formation. Oil and gas components form a single
broad peak. The water peak and oil/gas peak are nicely separated and are about
3 ppm apart, just as expected. The hydrate was assumed to be structure I methane hydrate. However, it was possible that some amount of other hydrate structure also existed due to the complexity of the black oil. There are some possible components in petroleum, such as methylcyclopentane, methylcyclohexane, neohexane, and adamantane, which can form some structure H hydrate with the help of methane. Of course the current technique described here is indifferent to the specific type of hydrate structures involved.

As mentioned before, the water peak area is linearly correlated with the amount of liquid water in the sample. As water turned into hydrate (and possibly also ice when the temperature was below zero), the water peak area decreased, as shown from Figure 9.3(a) to Figure 9.3(d). Peak areas were reproducible experimentally with an error of less than 1%. By measuring the change in peak area above the ice point, we can calculate exactly how much water in the emulsion has formed hydrate. From the rate of change of peak area, kinetic information can be obtained. To our knowledge, this is the first time that in situ hydrate behavior in black oil has been directly and so accurately measured.

The data for the experimental protocol described is shown in Figure 9.4 where the liquid water in the emulsion is plotted as a function of temperature. The liquid water content was obtained from the water peak areas after compensating for the general decrease in bulk magnetization due to the decrease in temperature. With reference to Figure 9.4, as the temperature of observation was decreased, no significant change in water content occurred until ~1°C. It should be noted that at 2000 psi, the methane hydrate equilibrium temperature in bulk water predicted by
CSMHYD is 16.34°C. Interestingly, after this initial onset, no more hydrate formed for 2 weeks at ~0°C, even though 70% of the water was still in the liquid state. A tempting explanation is that gas hydrate first occurred at the oil/water interface of the emulsion droplets. Because the diffusion rate of gas in hydrate solid is very slow, formation of hydrate shells around the droplets would keep gas from reaching the droplets wet interiors and prevent further hydrate formation.

![Graph showing the amount of liquid water in the sample as a function of temperature during hydrate formation and dissociation in black oil at 2000 psi.](image)

**Figure 9.4** The amount of liquid water in the sample as a function of temperature during hydrate formation and dissociation in black oil at 2000 psi.

Further cooling had no effect on the liquid water content until -15°C at which another drop occurred. About 10% of water still produced liquid signal even at -17°C. This second disappearance of liquid water was probably due to the formation of ice. Support for this conjecture was found when warming up – the lost liquid reappeared before the temperature reached zero. Ice formation/melting temperatures in water/oil emulsions are subject to Rayleigh depressions and dependent on droplet sizes. The melting temperature of ice crystallites in an emulsion would then be expected to
span some range related to the droplet size distribution. The amount of hydrate formation at subzero temperatures can be calculated from the difference between the formation and dissociation curves around -1°C. Subsequently, the amount of ice formation can be estimated by the total disappearance of liquid water at subzero temperatures deducted by the amount of hydrate formation at these temperatures. The water peak area reached a plateau above -2 °C. Hydrate started to show significant dissociation around 12°C, which is lower than predicted. This suggests the hydrate thermodynamic melting point was depressed by the same emulsion size considerations as for ice.

This experiment clearly demonstrates that NMR spectroscopy can directly detect and accurately measure hydrate behavior in black oil. Therefore, hydrate thermodynamics and kinetics can be obtained through this new technique. Using this technique and its extensions, future work will quantify the relations between hydrate behavior and emulsion droplet sizes and water cuts. This technique measures the conversion of liquid water within the emulsion in comparatively real time. By combining the technique with conventional pressure measurements, future studies will reveal information on the time lags inherent in pressure measurements and provide data on gas migration.

9.5 Conclusions

In this work, it was demonstrated that with adequate magnetic homogeneity the water peak can be distinguished from the black oil and gas peaks in proton NMR spectra. Because water in the solid hydrate phase is invisible to liquid state NMR spectroscopy, hydrate formation and dissociation in black oil were directly and
accurately observed for the first time by tracking the change of water peak area. Results illustrated that emulsion formation depresses both the ice point and the hydrate point in black oil. By providing a direct measure of hydrate information in black oil, this new technique offers great potential for equilibrium and kinetics studies that will benefit deepwater flow assurance.
Chapter 10. Summary of Contributions

Works were undertaken to address some key challenges in clathrate hydrate research. Contributions made in several areas are summarized below.

10.1 Molecular Mechanisms of Hydrate Formation and Dissociation

10.1.1 Residual Viscosity

Viscosities of tetrahydrofuran (THF)/H$_2$O=1/17 (molar ratio) mixture and natural gas/water system were monitored before hydrate formation and after hydrate dissociation using Champion Technologies Hydrate Rocking Cell (CTHRC) apparatus. Residual viscosity phenomenon was observed after natural gas hydrate dissociation under constant pressure, but it was absent after THF hydrate dissociation. Because natural gas hydrate dissociation involves mass transfer of a large amount of gas mass transfer through the water phase while THF hydrate does not have this complication, it was concluded that the residual viscosity reported in the literature is more likely due to higher than equilibrium gas concentration in the water phase after hydrate dissociation than residual clathrate hydrate structures.

10.1.2 Fluid Structure Change after THF Hydrate Dissociation

Proton spin-lattice relaxation time ($T_1$) and spin-spin relaxation time ($T_2$) of THF in deuterium oxide (D$_2$O) were measured before THF hydrate formation and after dissociation. Permanent changes in $T_1$ and $T_2$, indicators of local molecular orderings, were observed. It is known that local in-homogeneities in THF/D$_2$O solution exist even though they are macroscopically miscible. When it forms hydrate, THF molecules are uniformly distributed in the D$_2$O lattice. As hydrate dissociates, THF and D$_2$O are released into the liquid in a uniform manner. Therefore, it was
proposed that the $T_1$ and $T_2$ differences between before hydrate formation and after dissociation were due to a more homogenous THF/D$_2$O solution resulted from hydrate dissociation. This proposition can be further tested by Laser Light-Scattering study on the THF/D$_2$O solution after hydrate dissociation.

10.1.3 Influence of Hydrate Phase on the Coexisting Fluid Structure

Proton $T_1$ and $T_2$ of THF in D$_2$O were measured during hydrate formation and dissociation. It was found that $T_1$ and $T_2$ of THF in D$_2$O depended significantly on the phase fraction when the liquid was coexisting with hydrate phase at the THF/D$_2$O hydrate equilibrium temperature, which is $\sim 7.4 \, ^\circ$C as found out in this work. $T_1$ got longer and $T_2$ got shorter as more liquid phase was converted to hydrate. It was suggested that the hydrate phase influences the coexisting liquid fluid structure through long-range hydrogen bonding originated at the hydrate/water interface. The more the hydrate phase is present, the larger the fraction of the fluid structure being influenced, and consequently the longer the $T_1$ and the shorter the $T_2$ become.

10.1.4 Molecular Evidence of Residual Structure

$T_1$ measurements of THF in D$_2$O during hydrate transition repeatedly revealed that $T_1$ during hydrate dissociation was consistently higher than that during hydrate formation even though the solution was already homogenous before hydrate formation due to a previous hydrate formation/dissociation cycle. This demonstrated that the fluid structures during hydrate formation and dissociation were different. It was argued that this difference is the molecular evidence of residual clathrate structures lingering around in the liquid phase as a result of hydrate dissociation.
The $T_2$ results also showed a difference between hydrate formation and dissociation, but the difference was within experimental uncertainty.

### 10.1.5 $T_2$ Distribution of THF in Hydrate Cages

$T_2$ distribution measurement was applied to study the transition stage of THF/D$_2$O hydrate. For the first time, $T_2$ of THF in the hydrate phase was nicely captured as a peak in the $T_2$ distribution, totally separate from the signal arising from the coexisting liquid phase, with a value centered around 2-3 milliseconds. This technique can be potentially widely applied to gain understandings of other hydrate systems.

### 10.2 Gas Hydrate Behavior in Black Oil

Proton Nuclear Magnetic Resonance (NMR) Spectroscopy was innovatively employed to directly examine hydrate formation and dissociation behavior in black oil, which traditionally has always been indirectly measured by monitoring the pressure change. In this technique, a proton spectrum was taken for the water/methane gas/black oil system. It was demonstrated that water peak is easily distinguishable from the methane/black oil peaks in the spectrum and its area is directly related the amount of mobile liquid water in the sample. Since water in the hydrate phase does not show up in such spectra, the water peak area will decrease as hydrate forms and the quantity of hydrate formation can be calculated from the decreasing amount of water peak area. Therefore, in this work, hydrate formation and dissociation in black oil were directly and accurately measured by monitoring the water peak area in the proton NMR spectrum of the water/methane gas/black oil system. Results showed that hydrate formation stalls after initial onset without
external stirring. It was proposed that hydrate initially formed at the water/oil interface, this hydrate layer prevented gas from effectively coming in contact with liquid water, and consequently hydrate formation was slowed down. Liquid water was still present when the sample was cooled to –15 °C. Extension of this technique can be applied to obtain accurate hydrate thermodynamics/kinetics and gas migration data in black oil.
Chapter 11. Future Works

Results from this work have laid foundations and pointed out the directions for the following future works.

11.1 Extension of $T_2$ distribution technique to other hydrate systems

Because tetrahydrofuran (THF) is a large molecule and its behavior in hydrate cages can be captured by spin-spin lattice relaxation time ($T_2$) distribution technique, other smaller molecules that rotate faster than THF are likely able to be characterized by the same method. This includes the THF/H$_2$ hydrate, which is being pursued as a storage media for hydrogen energy. It would be interesting to see if the $T_2$ of CH$_4$ in D$_2$O hydrate can be measured using this technique. This $T_2$ distribution technique can also be potentially applied to study gas hydrates in black oil. A quick check of the feasibility of this would be to study whether $T_2$ distribution technique can detect ice formation in water/black oil emulsion.

11.2 Combination of NMR spectroscopy hydrate measurement and emulsion size distribution characterization

If the size distribution of water in oil emulsions can be dynamically characterized, along with the total amount of hydrate formation obtained from Nuclear Magnetic Resonance (NMR) spectroscopy, hydrate kinetics could be obtained. In a constant volume test, the delay between pressure change and the change of water peak area in NMR spectrum gives information about the gas migration rate in the oil phase.
11.3 $T_1 / T_2$ and diffusion measurements of liquid water during methane hydrate formation and dissociation

The results would give information about the structure of hydrogen bonding in the water phase and its dynamic evolvement during hydrate transition, which would be important contributions to the understanding of molecular mechanisms of hydrate formation and dissociation. These experiments would also answer the question whether the hydrate influence on the coexisting liquid phase is only unique in THF hydrate. ($T_1$ is the spin-lattice relaxation time.)

11.4 Diffusion measurements of CF$_4$ in liquid phase during hydrate transition

This experiment will complement the 11.3 measurements and the results will also generate significant insights on the molecular mechanisms of hydrate formation and dissociation.

11.5 Further investigate the activation energy change during the cooling process of THF/D$_2$O solution

Results on investigating the root causes for the slope changes $(\ln(1/T_1) - 1/T)$ and $(\ln(1/T_1) - 1/T)$ may yield information about the structural change of THF hydration shell structure and hydrate nucleation/formation mechanisms.
Appendix A. Basics of NMR/MRI

Independently developed by Felix Bloch\textsuperscript{125} and Edward Purcell\textsuperscript{126} in 1946, Nuclear Magnetic Resonance (NMR) is a powerful tool that can non-invasively detect molecular level dynamic and structural information. It has been widely applied in chemistry,\textsuperscript{127} medical,\textsuperscript{128} fluid dynamics,\textsuperscript{129} biology,\textsuperscript{130} food processing,\textsuperscript{131} and petroleum exploration,\textsuperscript{117} etc. Magnetic Resonance Imaging (MRI) is routinely being used in the medical field.\textsuperscript{128} The theories behind those applications are well established and complex. In-depth understanding can be challenging. Since NMR and MRI are heavily involved in this work, it is necessary to introduce the concepts of NMR/MRI, plus NMR relaxation processes and mechanisms. For complete descriptions of those concepts, other sources are available.\textsuperscript{11, 132, 133}

A.1 Basic Theory of Nuclear Magnetic Resonance

NMR refers to the response of atomic nuclei with intrinsic spins to magnetic fields. An atomic nucleus is commonly composed of both protons and neutrons. According to quantum mechanics, both protons and neutrons exhibit a magnetic moment and spin \( I = 1/2 \). The overall nucleus spin \( I \) may be zero, a positive integer or half integer based on the numbers of protons and neutrons it has. If the numbers of protons and neutrons are both even, \( I \) is zero. Then, the nucleus is invisible to NMR. \( I \) is an integer when both numbers are odd and is a half integer when one number is even and the other is odd. When a nucleus with a spin number \( I \) is placed in a magnetic field, it has an intrinsic angular momentum \( p \), which is a vector quantity with quantized orientation and magnitude. The magnetic moment \( \mu \) of a nucleus is
related to its angular momentum $p$ with proportionality constant $\gamma$, the so-called gyromagnetic ratio,

$$\mu = \gamma p$$  \hspace{1cm} (A.1)

Each kind of nuclei has a characteristic gyromagnetic ratio. For $^1\text{H}$, the value of $\gamma$ is $2.675 \times 10^8$ radian Tesla$^{-1}$sec$^{-1}$.

Each spin has a total number of $(2I+1)$ possible spin quantum states. Each state has its own spin quantum number $m$ in the range of $-l, -l+1, \ldots, l-1, l$ (listed in the order of decreasing energy and increasing stability). The nucleus that is of interest here is $^1\text{H}$, which has nuclear spin $l = \frac{1}{2}$. Therefore, $^1\text{H}$ has two quantum states corresponding to $m = -\frac{1}{2}$ and $m = \frac{1}{2}$. The energy associated with each state is,

$$E = -\mu \cdot \vec{B}_0 = -\gamma m \hbar B_0$$  \hspace{1cm} (A.2)

Where $\hbar$ is the Planck’s constant, $\gamma$ is the gyromagnetic ratio. Thus, the energy difference $\Delta E$ between states is,

$$\Delta E = \gamma \hbar B_0$$  \hspace{1cm} (A.3)

When spin with $m = \frac{1}{2}$ adsorbs this amount of energy, it will jump to $m = -\frac{1}{2}$ state. As the spin flips from $m = -\frac{1}{2}$ back to $m = \frac{1}{2}$ state, it will emit the same amount of energy. This is the so-called nuclear magnetic resonance. The resonance frequency $\nu_0$, also called Larmor frequency, can be inferred from quantum mechanical relation,

$$\Delta E = \hbar \nu_0$$  \hspace{1cm} (A.4)

Combine (A. 2) and (A. 3), we get,

$$\nu_0 = \frac{\gamma B_0}{2\pi}$$  \hspace{1cm} (A.5)
When a magnetic field is absent, quantum states \( m = 1/2 \) and \( m = -1/2 \) are equally likely. However if nuclei are subjected to magnetic field \( B_0 \), the population of nuclei in the lower energy \( (m=1/2) \) state will predominate. The ratio of populations of two states follows a Boltzmann distribution as a function of \( \Delta E \). This uneven distribution results in a net bulk magnetization \( M \) in the direction of magnetic field \( B_0 \).

In NMR experiments, there are two kinds of magnetic field, a strong static field \( B_0 \) pointing along \( +z \) direction and a weak radio frequency field \( B_1 \) rotating in \( xy \) plane at Larmor frequency. Application of \( B_1 \) for a period of time tilts the bulk magnetization off the equilibrium \( z \) direction by an angle \( \theta \). The bulk magnetization \( M \) processes around \( B_0 \) at an angular frequency \( \omega_0 \), as shown in Figure A.1,

\[
\omega_0 = \gamma B_0 \tag{A.6}
\]

Combination of (A.5) and (A.6) yields,

\[
\omega_0 = \frac{\nu_0}{2\pi} \tag{A.7}
\]

The resulting angle \( \theta \) is,

\[
\theta = \gamma t_p B_1 \tag{A.8}
\]

where \( t_p \) is the duration of the radio frequency pulse. The most common values of \( \theta \) in NMR experiments are 90° and 180°, which are separately called 90° and 180° pulses. After the removal of \( B_1 \), the spin will go back to its equilibrium state with the simultaneous emission of radio frequency energy. Consequently, \( M \) will recover back to \( +z \) direction, i.e. \( \theta \) becomes zero. This process is called relaxation. During this relaxation process, decaying magnetization \( M \) will induce an oscillating sinusoidal current in a receiver coil in the \((x, y)\) plane, which is recorded as a NMR signal.
A.2 NMR Relaxation

Macroscopically, NMR relaxation refers to the relaxation of bulk magnetization from excited state to equilibrium state. Microscopically, NMR relaxation is caused by interactions of spin with its environment and other spins.

A.2.1 Relaxation Process

Under a static magnetic field $B_0$, a sample with nonzero nuclear spin will gain a net magnetization with an equilibrium value $M_0$, which is parallel to $B_0$. Application of radio frequency pulse $B_1$ perpendicular to $B_0$ causes $M_0$ to tilt away from its equilibrium position. As a result, net magnetization in the $z$ ($M_z$) direction attains a new value and net magnetizations in $x$ ($M_x$), $y$ ($M_y$) directions become nonzero. These magnetizations start to relax after the removal of $B_1$. Relaxation of $M_z$ (parallel to $B_0$) is accompanied by energy exchange between spin and it's surrounding (referred as the lattice). Thus we call it spin-lattice relaxation or longitudinal relaxation. In most identical spin systems, spin-lattice relaxation is by-and-large a first order rate process. Spin-lattice relaxation is characterized by a time constant,
the spin-lattice relaxation time denoted as $T_1$. The recovery of $M_z$ back to $M_0$ can be described as

$$\frac{dM_z}{dt} = -\frac{M_z - M_0}{T_1} \quad (A.9)$$

The relaxation of transverse magnetizations, $M_x$ and $M_y$, involves no emission of energy. Both of them will relax to their equilibrium value zero in a first order rate manner by redistributing energy among spins. The spin-spin relaxation characteristic time constant $T_2$ is defined by

$$\frac{dM_x}{dt} = -\frac{M_x}{T_2} \quad (A.10)$$
$$\frac{dM_y}{dt} = -\frac{M_y}{T_2}$$

(A.9) and (A.10) are known as Bloch equations.

Inhomogeneity of the static magnetic field $B_0$, which is generally the case in real experiments, can affect $T_2$. Due to the inhomogeneity, spins at different locations “see” different magnetic fields. Thus, they precess at different frequencies according to their local magnetic field. This incoherence of spin motion causes additional transverse decay with a time constant $1/(\gamma \Delta B_0)$, where $\Delta B_0$ is the inhomogeneity of static field $B_0$. The observed transverse relaxation rate $1/T_2^*$ is,

$$\frac{1}{T_2^*} \approx \frac{1}{T_2} + \gamma \Delta B_0 \quad (A.11)$$

A.2.2 Nuclear Relaxation Mechanisms
As mentioned before, interactions of spin with its surrounding and other spins are responsible for NMR relaxation. Based on different features of interactions, there are several relaxation mechanisms.\textsuperscript{[11, 132]} For spin \( \frac{1}{2} \), there are three major relaxation mechanisms, spin rotation interaction, inter-molecular dipole-dipole, and intra-molecular dipole-dipole.

\textbf{A.2.2.1 Spin Rotation Interaction}

Spin rotation interaction is the dominant mechanism for gaseous state \( ^1\text{H} \). Because each nucleus has an electron cloud distribution, the rotation of nucleus produces a magnetic field. The strength of this magnetic field is proportional to the angular velocity of the nucleus. Molecular collisions cause the magnetic moment to fluctuate, resulting in a fluctuating magnetic field. This fluctuation of magnetic field causes the nuclear spin to relax. The smaller the moment of inertia, the more prominent this effect is. The spin-rotation interaction Hamiltonian is given by,

\[
H_{sr} = \hbar \mathbf{I} \bullet \mathbf{C} \bullet \mathbf{J}
\]

\[
\text{(A.12)}
\]

where \( \hbar \) is the plank constant, \( \mathbf{I} \) is the spin angular momentum operator of the resonant spin, \( \mathbf{C} \) is the spin rotation coupling tensor, and \( \mathbf{J} \) is the rotational angular momentum of the molecule.

Theoretical predictions of spin-lattice relaxations due to the spin rotation interaction are based on two models, a kinetic model for low densities and a diffusion model for high densities. For spherical-top molecule CF\(_4\), the kinetic model gives,

\[
\frac{1}{T_{1,\text{sr}}} = \frac{8\pi^2 I_{av} kT}{\hbar^2} \left( C^2_{av} + \frac{4}{45} \Delta C^2 \right) \tau_j
\]

\[
\text{(A.13)}
\]
the diffusion model gives,

\[
\frac{1}{T_{1,\text{sr}}} = \frac{8\pi^2 I_{av}kT}{\hbar^2} \left( C_{av}^2 + \frac{2}{9} \Delta C^2 \right) \tau_j
\]  

(A.14)

where, \( I_{av} \) is the molecular moment of inertia.

\[
C_{av} = \frac{1}{3} \left( C_{\parallel} + 2C_{\perp} \right)
\]  

(A.15)

\[
\Delta C = C_{\perp} - C_{\parallel}
\]  

(A.16)

where \( C_{\parallel} \) and \( C_{\perp} \) are spin rotation constants that characterize the coupling nuclear and molecular angular momenta along parallel and perpendicular axes.

**A.2.2.2 Dipole-Dipole Interaction**

Dipole-Dipole interaction contributes to spin relaxation when two spin \( \frac{1}{2} \) atoms are close enough to be affected by each other’s random fluctuating magnetic field, produced by magnetic dipoles. These local magnetic fields are modulated by random Brownian motions, i.e., ordinary thermal motion. Depending on whether the two spin \( \frac{1}{2} \) atoms belongs to the same molecule, this relaxation mechanism can be classified as inter-molecular dipole-dipole interaction or intra-molecular dipole-dipole interaction.

Assuming the molecular motion can be described as translation and rotational diffusions, McConnell\(^{133}\) derived the relation for dipole-dipole interaction by describing the molecular motion with a Langevin equation:

\[
\frac{1}{T_1} = I(I+1) \left\{ \frac{4}{3} j(\omega_s) + \frac{16}{3} j(2\omega_s) \right\}
\]  

(A.17)
where \( j(\omega) \) is the spectral density. The evaluation of this spectral density depends on the types of dipole-dipole interaction and the particular model chosen to describe the thermal motion.

**Inter-molecular Dipole-Dipole Interaction**

Dipole-Dipole interaction with nuclei in neighboring molecules is called inter-molecular dipole-dipole interaction. The random local fluctuating magnetic field for inter-molecular dipole-dipole interaction generally arises from random translational motions of the molecules.

In the extreme narrowing limit, based on equation A.17, the Brownian motion model gives,

\[
\frac{1}{T_{1,\text{inter}}} = \frac{8\pi n \nu^4 \hbar^2 I(I + 1)}{15D\sigma} \tag{A.18}
\]

where \( n \) is the number density, \( \nu \) is the number of resonant nuclei in a given molecule, \( \hbar \) is the Plank's constant divided by \( 2\pi \), \( I \) is the spin number, \( D \) is the translational diffusion constant, \( \sigma \) is the molecular diameter.

**Intra-molecular Dipole-Dipole Interaction**

If the dipole-dipole interaction arises from two nuclei on the same molecule, it is classified as intra-molecular dipole-dipole interaction. For a rigid molecule, the dipole-dipole relaxation is caused by molecular rotation. Assuming the molecular reorientation motion decays exponentially with correlation time \( \tau_c \), the relaxation times for like spin dipole-dipole interactions are given as follows,

\[
\left( \frac{1}{T_1} \right)_{\text{intra}} = M^2 \frac{2}{3} \left\{ \frac{\tau_c}{1 + \omega^2 \tau_c^2} + \frac{4\tau_c}{1 + 4\omega^2 \tau_c^2} \right\} \tag{A.19}
\]
\[
\left( \frac{1}{T_2} \right)_{\text{intra}} = M_2 \frac{1}{3} \left\{ 3 \tau_c + \frac{5\tau_c}{1 + \omega^2 \tau_c^2} + \frac{2\tau_c}{1 + 4\omega^2 \tau_c^2} \right\}
\]

where \( M_2 \) is a constant and its value depends on the type of molecule, \( \omega \) is the resonance frequency, \( \tau_c \) is the rotational correlation time. The intra-molecular dipole-dipole interaction is significant only for the nearest neighbors because the coefficient, \( M_2 \), is a function of spin-spin distance to the inverse sixth power.

In short correlation time region, the molecular orientation changes rapidly, i.e., \( \omega \tau_c \ll 1 \). In this case,

\[
\frac{1}{T_1} = M_2 \frac{10}{3} \tau_c \quad \text{(A.21)}
\]

\[
\frac{1}{T_2} = M_2 \frac{10}{3} \tau_c \quad \text{(A.22)}
\]

In long time correlation region, the molecular orientation changes slowly, i.e. \( \omega \tau_c \gg 1 \). Then,

\[
\frac{1}{T_1} = M_2 \frac{4}{3\omega^2} \frac{1}{\tau_c} \quad \text{(A.23)}
\]

\[
\frac{1}{T_2} = M_2 \tau_c \quad \text{(A.24)}
\]

### A.2.3 Measurements of Relaxation Times

There are several ways to measure \( T_1 \) and \( T_2 \) relaxation times. Only the methods that will be used in this work are mentioned here.
A.2.3.1 Measurement of $T_1$

The most common method to measure $T_1$ is the inversion recovery (IR) method. The pulse sequence in inversion recovery method is as following. Initially, a 180° pulse along x axis is applied to invert $M_0$ from $+z$ to $-z$ direction. Then after a time period $t$, during which $M_0$ relaxes to $M_z$, a 90° pulse along x-axis tilts $M_z$ to y-axis. At this point, the free induction decay is recorded. The initial magnitude of the free induction decay (FID) is proportional to $M_z$. This process is schematized in Figure A.2. With the initial condition $M_z = -M_0$ at $t=0$, for a single type of spin, $M_z$ can be described as,

$$M_z = M_0 \left( 1 - 2e^{-t/T_1} \right) \quad \text{(A.25)}$$

The same experiment is repeated 40 to 50 times with different delay time $t$. The plot of $\ln[(M_0-M_z)/2M_0]$ vs $t$ will yield a straight line of slope $-1/T_1$.

A.2.3.2 Measurement of $T_2$

The most commonly used and the most accurate method for $T_2$ measurement is the Mieboom-Gill modification of the Carr-Purcell (CPMG). In a CPMG sequence, a 90° pulse is applied along the x-axis at time zero to flip $M_0$ to the y-axis. Because of the magnetic field inhomogeneity, the spins in higher field (spin type F) precess faster than the ones at lower field (spin type S). Due to this incoherent motion, the spin isochromats start to dephase. After a time period $\tau$, an 180° pulse is applied along y-axis. A spin echo forms along y-axis at time 2 $\tau$. 180° pulses are applied along y-axis again at time 3$\tau$, 5$\tau$, 7$\tau$, ..., and spin echoes form at 4$\tau$, 6$\tau$, 8$\tau$, ... The CPMG sequence is illustrated in Figure A.3.
Each spin echo magnitude is recorded. For a sample composed of a single type of spins, the magnetization is correlated with time $t$ in the following equation,

$$M(t) = M_0 e^{-t / T_1} - \gamma G^2 D \frac{t^2}{3}$$  \hspace{1cm} (A.26)

where $G$ is the magnetic field gradient due to the inhomogeneity of magnet, $D$ is the diffusion constant. Therefore, the observed spin-spin relaxation rate $1/T_2^*$ is,

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \gamma^2 G^2 D \frac{\tau^2}{3}$$  \hspace{1cm} (A.27)

For a slow diffusing sample, the diffusion term can be eliminated by making $\tau$ very small. In that case, the observed $T_2^*$ approximately equals the real relaxation time $T_2$. 

**Figure A.2** Inversion recovery sequence.
Figure A.3 CPMG sequence.
Figure A.3 CPMG Sequence (continued).

A.3 Molecular Diffusion

Several techniques are available to measure self-diffusion constants. Compared to traditional radioactive tracer techniques, NMR measurements of self-diffusion coefficients are easier and faster and give true self-diffusion rates. The early NMR self-diffusion measurements used the Carr-Purcell (CP) method, which has several limitations.\textsuperscript{[134]} Currently the most widely used method is Stejskal-Tanner (ST) pulsed gradient NMR technique.\textsuperscript{[135]} Compared to CP, the ST method gives
better signal to noise ratio, permits the measurement of restricted diffusion, and can measure values of D down to $10^{-9}$ cm$^2$/s, instead of $10^{-7}$ cm$^2$/s.

![Diagram showing pulse gradient spin-echo method](image)

**Figure A.4** Sequence of pulse gradient spin-echo method.

As described in Figure A.4, in the ST method, a 90° pulse is first applied to flip the magnetization to y-axis, and the spin isochromats (microscopic ensembles of spins that experience the same magnetic field) start to dephase due to the inhomogeneity of static magnetic field. After certain period of time, a magnetic field gradient of strength g and duration δ is applied to accelerate the spins dephasing rate. After the cutoff of this magnetic gradient, the spins resume normal relaxation rate. Then an 180° pulse is applied to flips the spins to reverse the direction of dephasing. A second identical gradient pulse is applied after the 180° rf pulse to accelerate the dephasing rate. The time interval between two rf pulse is $\tau$, and the time between two gradient pulses is labeled $\Delta$. A spin echo occurs at time $2\tau$. If the molecules don’t diffuse, there is no loss in the echo amplitude. However, if the molecules do move to a different region, they will precess at frequencies different from previous ones. Therefore, the refocusing will be incomplete. As a result, the spin echo amplitudes sequentially decrease.
For unbounded diffusion, the random walk motion of molecules can be described as a probability function $P(r_0 | r, t)$. $r_0$ is the initial position of a molecule, and $r$ is its position after the time interval $t$. Fick’s law gives that,

$$P(r_0 | r, t) = (4\pi Dt)^{-1.5} e^{-\frac{(r-r_0)^2}{4Dt}}$$ \hspace{1cm} (A.28)

where $D$ is the self-diffusion coefficient. If the diffusion of a nuclear spin follows the above relation, the spin echo height attenuation $R$ for the pulse gradient experiment is given by

$$R = \frac{M}{M(0)} = e^{-\gamma^2 \delta^2 g^2 (\Delta - \delta/3)}$$ \hspace{1cm} (A.29)

where $\gamma$ is the spin gyromagnetic ratio, $M$ is the echo height with applied gradient $g$, and $M(0)$ is the echo height when the gradient is off. $\delta$, $g$ and $\Delta$ can be varied experimentally.

The diffusion constant can be experimentally acquired by plotting $\ln(R)$ vs. $-\gamma^2 \delta^2 g^2 (\Delta - \delta/3)$. The slope of this linear plot is the diffusion coefficient.

**A.4 Magnetic Resonance Imaging (MRI)**

MRI is the imaging application of NMR, which is able to vividly define the internal structures of appropriate objects in great detail without any intrusive damage. Doctors all around the world are routinely employing it as the most effective diagnostic tool for certain diseases. It revolutionized the medical imagining industry and touched the lives of many. In the scientific community, MRI opened researchers’ eyes to nature’s untouched secrets and propelled our scientific knowledge to an unprecedented stage.
The fundamental basis of MRI is that a spin's NMR resonance frequency $\nu$ is proportional to the magnetic field $B_o$ it experiences, i.e., spins at different positions in a spatially varying field will resonate at different frequencies.

$$\nu = \gamma B_o$$  \hspace{1cm} (A.30)

$\gamma$ is the gyromagnetic ratio. Therefore, in magnetic fields with known gradients, the spectrum of a sample from such fields gives the number of spins that are experiencing different frequencies. Consequently, this information gives the number of spins at different locations of a sample, i.e., the contour of an object, as demonstrated in Figure A.5.\textsuperscript{[11]}

![Diagram showing the relationship between increasing $B_o$, frequency, intensity, sample, and spectrum.]

**Figure A.5** Acquisition of a one-dimensional NMR image.

In practice, this slice selection is achieved by applying a one-dimensional, linear field gradient during the period when the Radio Frequency (RF) pulse is on. This RF pulse applied in conjunction with a magnetic field gradient will rotate only
the spins that are located in a slice or plane through the object by the required amount. Assuming the gradient is along z direction, the location of the slice with respect to the isocenter is given by,

\[ Z = \frac{\nu - \nu_o}{\gamma G_z} \]  

(A.31)

\( \nu \) is the resonance frequency at the selected slice, \( \nu_o \) is the resonance frequency at the position where the field strength is \( B_0 \), i.e., isocenter, \( G_z \) is the magnitude of the field gradient along z direction.

Unlike conventional scattering experiments where spatial information comes from interference of waves with different point centers, the spatial resolution of MRI is not determined by the magnetic wavelength. In MRI, the spatial information of objects is contained in the frequency domain since the slice selections are realized by applying magnetic field gradients. Therefore, it is possible to achieve better spatial resolution by using larger field gradients and by collecting data repeatedly over longer time ranges. Due to the hardware limitations, current spatial resolution achievable is in the region of 5\( \mu \)m.\textsuperscript{[11]}

There are several imaging reconstruction methods, such as back projection and iterative reconstruction. The software package of the MRI system used in this work employs the Fourier reconstruction technique, which is widely employed in present day MRI tomography.

A.4.1 Fourier Imaging in Two Dimensions

In obtaining two-dimensional images, a shaped RF pulse is initially applied in the presence of a magnetic gradient to excite the spins in a selected slice. Assuming
the magnetic gradient is in the z direction, the selected slice is in the x-y plane. Subsequently, phase encoding gradients of $G_x$ and $G_y$ in the x and y directions are applied consecutively or concurrently for time durations of $t_x$ and $t_y$. In the rotating frame, for a spin at position $r$ in the selected x-y plane, the phase angle changed by such gradients is given by,

$$\phi(r) = \gamma (xG_xt_x + yG_yt_y)$$  \hspace{1cm} (A.32)

This relation can be expressed as:

$$\phi(r) = (\gamma G_xt_x + \gamma G_yt_y) \cdot (x i + y j) = k \cdot r$$  \hspace{1cm} (A.33)

The transverse magnetization signal from this position is then proportional to $\exp[ik \cdot r]$.

Suppose the density distribution of spins in the selected x-y plane as a function of position is $\rho(r)$, the transverse magnetization of the entire slice can be calculated by integrating the signal over the density distribution,

$$F(t) = \int_{\text{slice}} \rho(r) \exp(ik \cdot r) d^2r$$  \hspace{1cm} (A.34)

This Fourier transform relation indicates the signal corresponding to a particular set of $G_x$, $t_x$, $G_y$, $t_y$ gives the Fourier transform of the density function $\rho(r)$ at a single point in $k$-space. After collecting enough data in $k$-space by varying combinations of $G_x$, $t_x$, $G_y$, $t_y$, the following discrete two-dimensional (inverse) Fourier transform can be performed to reconstruct the image,

$$\rho(r) = \frac{1}{(2\pi)^2} \int F(k) \exp(-ik \cdot r) d^2k$$  \hspace{1cm} (A.35)
The basic procedure for implementing two-dimensional Fourier imaging is illustrated in Figure A.6.[11] Different imaging techniques differ in the manner how the \( k \)-space is covered.

![Diagram illustrating two-dimensional Fourier imaging](image)

**Figure A.6** Two-dimensional Fourier imaging in x-y plane.

### A.4.2 Fourier Imaging in Three Dimensions

Since a three-dimensional image requires spatial information of every point in the sample, the image acquisition starts with a broad band excitation pulse so that transverse magnetization is created for the entire volume of the specimen. Subsequently, phase encoding gradients of \( G_x \), \( G_y \), and \( G_z \) are applied, consecutively or concurrently, in the x, y, and z directions respectively for time durations of \( t_x \), \( t_y \), and \( t_z \). In the rotating frame, for a spin at position \( r \) with coordinates \( (x, y, z) \) in the object, the phase angle changed by such gradients is given by,
\[ \phi(r) = \gamma (xG_x t_x + yG_y t_y + zG_z t_z) \]  

(A.36)

This relation can be expressed as:

\[ \phi(r) = (\gamma G_x t_x i + \gamma G_y t_y j + \gamma G_z t_z l) \cdot (x i + y j + z l) = k \cdot r \]  

(A.37)

The transverse magnetization signal from this position is then proportional to \( \exp[ik \cdot r] \).

Suppose the density distribution of spins in the entire specimen as a function of position is \( \rho(r) \), the transverse magnetization of the overall volume can be calculated by integrating the signal of each point in the density distribution,

\[ F(t) = \int_{\text{volume}} \rho(r) \exp(ik \cdot r) d^3r \]  

(A.38)

This Fourier transform relation indicates the signal from a particular set of \( G_x, t_x, G_y, t_y, G_z, t_z \) gives the Fourier transform of the density function \( \rho(r) \) at a single point in \( k \)-space. After collecting enough data in \( k \)-space by varying combinations of \( G_x, t_x, G_y, t_y, G_z, t_z \), the following discrete three-dimensional (inverse) Fourier transform can be performed to reconstruct the image,

\[ \rho(r) = \frac{1}{(2\pi)^3} \int F(k) \exp(-ik \cdot r) d^3k \]  

(A.39)

The implementing procedure of the three-dimensional image acquisition is illustrated in Figure A.7. After the application of the gradients, data for the transverse signal may be collected.

For details about implementing the two- and three-dimensional Fourier imaging process, consult Cowan\(^{(11)}\) for a complete description.
Figure A.7 Three-dimensional Fourier imaging.
Appendix B. Operations of NMR/MRI Apparatus

This appendix details the procedures for obtaining relaxation times and images using the 85MHz super-conducting horizontal magnet from Oxford Instruments and the 2MHz tabletop MARAN spectrometer from Resonance Instruments. The software package for the high field super-conducting magnet is from Varian, called VNMRS. The acquisition program for MARAN is RINMR and the data processing software is WinDXP. Some of the following materials are summarized from the reference materials provided by the software vendors.

B.1 Spin-Lattice Relaxation Time ($T_1$) Measurements (85MHz)

Stage one: Turn on the system

1. Switch the cooling water valve to the “ON” position.
2. Push the power button on the chiller to the “ON” position.
3. Check on the water pressure. It should be around 45psi. High water pressure can cause leaking problem.
4. After the temperature of the cooling water reached the desired value, which is marked by a black line, it is time to turn on the NMR hardware.
5. Turn the power switch on the gradient amplifier to the “ON” position.
6. Push the “Start” button. The indicator should read 0.03.
7. Switch the power bar for water-cool of the shimming system to “ON” position.
8. Turn on the shimming system. The power button is located on the lower right corner of the panel.
9. Pay attention to the temperature of the cooling water that flows out of the system and make sure it is not too high. A black line on the thermometer marks the desired value.

10. Make sure the terminal computer is on. Log in and open the “VNMR” program.

Stage Two: Tuning the probe

1. Set “tn = H1”.

2. Type “su” in the command window.

3. Disconnect the cable from the probe port and connect it to the tune port.

4. Press the channel selection button to read “1”.

5. Set the attenuation to level “8”. If it is way off scale, change it to a lower value so that the full range of the reading is properly displayed.

6. Connect the two rods to the “tune” capacitor and the “match” capacitor respectively.

7. Turn the “tune” and “match” capacitors back and forth to minimize the reading to less than 5.

8. Change the channel selector to 0.

9. Disconnect the probe cable from the “tune” port and connect it to the “probe” port.

Stage Three: Calibrating the 90° and 180° pulses

1. Acquire a proton spectrum using s2pul macro s2pul (Figure B.1) and phase the NMR peak of interest.
Figure B.1 S2pul pulse sequence. \( p_1 \) and \( pw \) are pulse lengths; \( d_1 \) and \( d_2 \) are delay times. In \( T_1 \) measurements, \( p_1 \) is 180° pulse; \( pw \) is 90° pulse; \( d_1 \) is the delay time between two measurements (typically \( d_1 \geq 5T_1 \)); \( d_2 \) is the spin recovery time.

2. Type "nt=1, gain="y", ai, vp=50" in the command window, which mean the number of scans is 1; receiver gain is set to value in stored experiment; set absolute intensity mode; spectrum vertical position = 50.

3. Set \( p_1 \) to zero.

4. Have your best guess about the length of the 360° pulse and assign an array of values around it to \( pw \) using the array command.

5. Assign a value that is close to a 90° pulse to \( pw[1] \) in order to phase correctly the collected spectra. It will be hard to accurately phase the spectra obtained around 360° pulse because their magnitudes are very small.

6. Set the \( d_1 \) to a value that is long enough to allow spins to fully relax before the application of next pulse.

7. Type au in the command window to submit experiment for acquisition and process data.
8. After the first spectrum data is collected, type \texttt{wft(1)} (weighted Fourier transform), \texttt{aph} (automatic phasing), \texttt{vsadj} (automatically adjusts the vertical scale to fit the screen with the tallest peak of the spectrum).

9. After the data acquisition is completed, type \texttt{wft dssh} to perform weighted Fourier transform on all the data and display the spectra stacked horizontally.

10. Examine the displayed spectra to check if the spectra series starts negative from the second spectrum and passes through a null point to increasingly positive values.

11. If yes, estimate the location where the spectrum becomes zero. This is the point for 360° pulse.

12. If not, assign a new array of data to \texttt{pw} based on the result just obtained and go through step 5 to step 10 again. Repeat this process until the 360° is found.

13. From the 360° pulse, 90° and 180° pulses can be obtained. $P(90°)=P(360°)/4$, $P(180°)=P(360°)/2$.

Stage Four: Perform $T_1$ measurements

1. Under the S2pul sequence, assign the calibrated 180° and 90° values to \texttt{p1} and \texttt{pw} respectively.

2. Type “ai” in the command window to chose the absolute intensity mode.

3. Type \texttt{dot1} in the command window to interactively allow the program to automatically set up \texttt{d1} and \texttt{d2} parameters by entering the minimum $T_1$ expected, the maximum $T_1$ expected, and the experiment time.
4. Type `ga` to start the acquisition.

5. After acquisition is completed, type "ds(arraydim)" to display the last spectrum.

6. Phase the spectrum and place the threshold line so that all the unwanted peaks are below it.

7. Type "dll" and "fp" in the command window. Make sure only the peaks of interest are listed. If the spectrum is in stacked mode, type "full" to change to full mode.

8. Type "dssh" to display the stacked spectra horizontally.

9. Type "t1" to automatically calculate the $T_1$'s. All the calculated values are displayed in *dg* window.

10. To view the exponential fits and the experimental data in graphs, type "expl".

11. If this measured value is outside the initial guess, repeat steps 3 – 10 until the measured value is within the initial guesses for maximum and minimum $T_1$'s and the error is minimized.

12. Type "svf" to save the data.

**B.2 Magnetic Resonance Imaging (MRI) Measurements (85MHz)**

Stage one: Turn on the system

Refer to $T_1$ measurement procedure for details.

Stage two: Tuning the probe

Refer to $T_1$ measurement procedure for details.

Stage three: Calibrating the 90° and 180° pulses
Refer to $T_1$ measurement procedure for details. After getting the correct pulse lengths, supply the values using the "pulsecal" command. The pulse pattern would be "square".

Stage four: Determining the reference offset frequency

1. In EXP1, acquire a proton spectrum using s2pul and type "ds" to display it.
2. Put the cursor near the highest point of the peak in the spectrum and type "nl" and "offset".
3. Record this number for setting the "resto" in imaging experiment.

Stage five: Setting up the imaging parameters

1. Join an available experiment by typing "jexp#". # is the number of the experiment you want to join.
2. Retrieve the Spin-Echo Multi-Slice (SEMS) parameters by entering the command "sems". If a similar experiment has been done before and saved on the computer, the parameters can be retrieved by loading the experimental data through the menu system. This sequence comprises of a 90 degree RF pulse followed by a 180 degree refocusing pulse, both applied in the presence of a slice select gradient.
3. Make sure "gcoil = main". gcoil parameter holds the name of the gradient calibration table.
4. Set "pilot = y" to ensure that all the refocusing parameters are properly computed within the pulse sequence.
5. Set "resto" to the reference frequency obtained in Stage four. This parameter's function is to make sure that all positions are properly referenced to the center of the magnet and gradients.

6. Set the slice thickness by assigning "thk" to an appropriate value. 2mm or 3mm is a good place to start.

7. Select the image orientation by setting "orient" to "trans" (transverse – Z slice gradient), "sag" (sagittal – X slice gradient), or "cor" (coronal – Y slice gradient). "cor" was chosen in this study based on the geometry of the sample.

8. Set "pss", the slice positions relative to the gradient origin, which is in the unit of centimeter. This parameter automatically decides the value of "ns", the number of slices.

9. Set the Field of View parameters, "lro" – length in read out direction (cm); "lpe" – length in phase encoding direction (cm).

10. Check that "seqcon = 'ncsnn'" for proper multi-slice operations in SEMS.

11. Choose appropriate values for "tr" and "te" (both in seconds). "tr" is the time between two successive excitation of one slice, i.e., the repetition time. In the case of 90° pulse excitation, "tr" should be about 5T₁. "te" is the echo time, the time from the application of the RF pulse to the peak of the signal (the echo) induced in the coil.

12. Set "tspoil", spoiler gradient time that is applied to suppresses the free induction decay signal to make short "te" possible.
13. Assign appropriate values to “np” – number of points in read out direction, “nv” – number of steps in phase encoding, “nt” – number of transient averages.

14. Set “dp” to “y”.

Stage six: Check the readout projection

1. Type “nv = 0”.

2. Enter “imprep”. This command takes the information about the RF coil, the slice thickness, and the selected field of view, and it automatically computes and sets the parameters gro, gpe, gss, tpwr1, tpwr2, and sw.

3. Ignore the warning and a message will be displayed, “setup complete”.

4. Enter “ga” to run the experiment.

5. If the resulting projection is off-center, put the cursor where you want the new center to be and enter “movepro”. This computes a new value for the “pro” readout position parameter, which sets the proper frequency during data acquisition.

Stage seven: Acquire the image

1. After making sure that the readout projection is properly centered, assign the appropriate value to “nv” (typically 128 or 256).

2. Enter “imprep”.

3. After getting the message “setup complete”, enter “go” to start the acquisition.

4. When the image acquisition is complete, enter “ft2d” to see the result.

5. Enter “svib” to save the image, or “svf” to save the FID.
B.3 Spin-Spin Relaxation Time ($T_2$) Measurements (2MHz)

Stage one: Calibration

1. Place the mineral oil calibration sample inside the NMR and adjust the position to the “sweet spot”.
2. Open the “RINMR” program from the terminal computer.
3. Click on “Acquisition”.
4. Click “Pulse Sequence” – “Load” – “wobble.exe”.
5. Turn the switch in the back of the equipment from “normal” to “wobble” position.
6. Type in “GS1” to execute the wobble program.
7. Go to “View” – “Magnitude”.
8. Make sure that the center of the parabola aligns with the vertical line in the center of the calibration window. If not, use the special screwdriver to adjust the equipment.
9. Enter “stop” in the command line.
10. Turn the switch in the back from “wobble” to “normal”.
11. Enter “.AUTO01” in the command line to automatically set up the frequency offset (O1).
12. Load “Train 90” from “Pulse Sequence” – “Load”.
13. Enter “GS1” and “P90” consecutively in the command line.
14. Use the PgUp or PgDn to make the bars lay as close as to x-axis.
15. After having a good match, record the “P90” value and enter “Stop”.
16. Load “Train 180” from “Pulse Sequence” – “Load”.

17. Follow steps 14 to 16 and replace "P90" with "P180" in the steps.

18. Record "P180" value.

19. Enter the "P90" and "P180" values in the "Acquisition Parameter".

Stage two: Data acquisition

1. Load the "cpmg" pulse sequence.

2. Adjust the values in "Acquisition Parameter" according the needs of certain particular experiment, such as "NS" – Number of Scans; "RD" – Relaxation Delay (μs); "ECH" – Number of Echoes; "RG" – Receiver Gain (%).

3. Place the sample in the "Sweet Spot" of the magnet.

4. Enter "Go" to start the acquisition.

5. Save the data after the acquisition is complete.

Stage three: Data processing

1. Open "WinDXP".

2. Load the raw NMR data.

3. Click on the "Fit Data" icon to process the data.

4. Save the results after the fitting is complete.

5. Both the NMR data and the fitted data can be exported to excel by clicking "File" – "Export Data".
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