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Studies On Structure And Dynamics In Clathrate Hydrates

By

Luyi Ding

**A THESIS SUBMITTED TO
THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCES**

**OTTAWA-CARLETON CHEMISTRY INSTITUTE
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Studies On Structure And Dynamics In Clathrate Hydrates

Submitted By Luyi Ding

In Partial Fulfilment of The Requirements for The Degree of
Master of Science

Thesis Supervisor

Chairman, Department of Chemistry

Carleton University

1995

Abstract

Clathrate hydrates, a class of inclusion compounds, have an unusually long scientific history, and hence are considered to be a relatively mature research subject. However, over the years new results continue to appear, challenging both earlier theory and experiments.

The existence of clathrate hydrates has been confirmed in permafrost, on the sea floor and in glaciers, and there have been speculations concerning clathrate hydrate existence in other parts of the solar system, as well as in the galaxy. Since formaldehyde is one of the more abundant interstellar gases, and polyoxymethylene was the first extraterrestrial polymer identified, it is likely that the formaldehyde hydrate exists in icy extraterrestrial environments. Experimental results show that the deposition of formaldehyde gas along with water vapour at low temperatures does allow a clathrate hydrate to form. X-ray powder diffraction results show the formaldehyde hydrate to be of the structure I type. The ^2H NMR lineshape of pure solid formaldehyde- d_8 is quite different from the lineshape of formaldehyde encaged in the clathrate hydrate cages. The molecular motion of formaldehyde in the pure solid and in the hydrate cage were also studied by the variable temperature ^2H NMR technique. Formaldehyde hydrate is the first example of a clathrate hydrate of astrophysical significance which can not be made under terrestrial conditions. The vapour co-deposition at low temperature is a good generation technique for novel and unusual hydrates.

The inhibition of hydrate formation is another current and interesting topic in the study of hydrates. Recently, attention has switched from thermodynamic inhibitors such as methanol to polymers such as poly(N-vinylpyrrolidone) and poly(N-vinylcaprolactam) which are thought to be kinetic inhibitors. Such polymers are considered good alternatives to current thermodynamic inhibitors since they are non-toxic and only a small amount (0.5 w/w %) is required. Results of macroexamination show that the kinetic inhibitor affects the hydrate formation time and hydrate appearance. The X-ray powder diffraction results show that the kinetic inhibitors, poly(N-vinylpyrrolidone) and poly(N-vinylcaprolactam) do not alter the hydrate structures. Solution ^1H NMR spectroscopy is used to study the distribution of the kinetic inhibitors; it is found that these inhibitors are equally associated with the solid hydrate and liquid phases. ^1H NMR spectroscopy results also reveal that the addition of kinetic inhibitor at low concentration does not change the hydrogen bonding of water in the solution from which hydrates crystallize. The experimental results show that kinetic inhibitors behave quite differently when compared with thermodynamic inhibitors, such as methanol. It is the first time that ^1H NMR has been used to study the mechanism of kinetic inhibition. The results presented are consistent with a surface blocking mechanism.

Acknowledgments

I thank all the people who have helped me during my studies at the Department of Chemistry, Carleton University, either with moral encouragement or helpful technical assistance. The facilities of the Molecular Structure and Dynamics group of National Research Council made this research possible.

I wish to express my deepest acknowledgment to my supervisor, Professor, Dr. John A. Ripmeester. Without his instructive supervision, I would not have undertaken to complete this thesis. I was lucky to be his student. I am deeply impressed by his professional attitude towards science, his vast knowledge, and his dedication to science research. I am grateful for his helpful comments and guidance throughout the course of this thesis and the numerous hours he spent suggesting changes to this thesis. I am thankful for his patience and persistence in assisting me to accomplish this work.

To my fellow graduate students and research associates at the Steacie Institute for Molecular Sciences, National Research Council, thanks for the support and friendship. To E. B. Brouwer, my classmate, thanks for the generous, great help and always friendly smile during the course of my struggle. To X. Zhu, I. L. Moudrakovski, H. Nakayama, G. Lee, thank you for many helpful discussions

I would like to thank the first rate scientists and support staff in the MS&D group of SIMS, NRC. Thank to Drs. C. I. Ratcliffe, D. D. Klug, J. S. Tse, K. F. Preston for all their help. Thanks also go to J. T. Bennett, G. McLanrin, R. Dutrisac and M. Vandenhoff for helpful technical assistance.

I also acknowledge the financial support of Carleton University and Professor E. D. Sloan, Jr. of Colorado School of Mines.

Finally, I would like to give my deepest thanks to my family for their support and patience in this undertaking.

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List of Abbreviations

A	Angstrom, 10^{-10} m
B_0	external magnetic field
C_{jm}	Langmuir type constant for a guest molecule j in a type m cavity
d_{hkl}	value of the interplanar spacing
D_2CO	deuterated formaldehyde
D_2O	deuterated water
efg	electric field gradient
eQ	electric quadrupole moment
E_a	activation energy
FID	free induction decay
fml	fast motion limit
f_j	fugacity of the gas component j in the hydrate phase
H	Hamiltonian operator
2H	deuterium
HSZ	hydrate stable zone
I	spin angular momentum operator
K	temperature (Kelvin)
k	Boltzmann's constant
MeOH	methanol, CH_3OH

MEG	monoethylene glycol
nm	nanometer
NMR	nuclear magnetic resonance
PAS	principal axis system
POM	polyoxymethylene
PVCap	poly(N-vinylcaprolactam)
PVP	poly(N-vinylpyrrolidone)
q	electric field gradient
r_{ij}	internuclear distance
RF	radio frequency
THF	tetrahydrofuran
TMS	tetramethylsilane
TREOR	TRial-and-ErrOR indexing program
T_2	spin-spin relaxation time
μ	magnetic moment
$\mu_w(h^0)$	chemical potential of water in hypothetical empty hydrate
$\mu_w(h)$	chemical potential of water in occupied hydrate
v_m	number of cavities of type m per water molecule in the unit cell
θ_{jm}	occupancy of cavity m by component j
$\Delta\mu_w^0$	chemical potential of the empty lattice relative to ice
γ	gyromagnetic ratio
$\hbar$	Planck's constant divided by 2π .

ω_0	Larmor frequency.
σ	chemical shielding tensor,
η	asymmetry parameter,
χ	quadrupolar coupling constant
δ_{ppm}	chemical shift

Chapter I

General Description of Clathrate Hydrates

1.1 Introduction

Clathrate hydrates, traditionally referred to as gas hydrates, are solid crystalline compounds formed when certain small molecules come into contact with water near its freezing point. Hydrogen-bonded water molecules form cavities or voids which can accommodate molecules of suitable size. Inclusion of these “guest” molecules causes enough molecular interaction to stabilize the otherwise metastable water lattice structure.

The first hydrate was discovered by Davy in 1811. He reported the formation of a yellow ice-like material as a result of chlorine gas bubbling through water.¹ The field lay largely dormant until the period 1880-1910 when Villard and de Forcrand, as well as others, investigated a large number of natural gases that formed hydrates (i.e., CH₄, CO₂, C₃H₈, etc.).² Initially, hydrate studies were purely academic until the 1930s when it was discovered that hydrates could form in natural gas pipelines and effectively block the gas flow,³ and research was focused on devising methods to prevent hydrate formation in gas pipelines in cold regions.

The modern investigations of clathrate hydrates began with the work of von Stackelberg and coworkers,⁴ Claussen,⁵ and Pauling and Marsh⁶ around 1950. They showed that the gas hydrates were clathrate compounds, and determined the two types of gas hydrate structures by X-ray diffraction (cubic structure I and structure II). In 1960, Jeffery and co-workers redetermined the structure I and structure II hydrate. They also

began a program of determining the structure of a large number of amine and ammonium salt hydrates in which the amino groups are generally linked by hydrogen bonds to water molecules and hence termed “semi-clathrate hydrate”.^{10,11}

Structures I and II were thought to be the main clathrate hydrate structures (though there were some other structures such as the Tetragonal structure specific to Br₂³⁰ and dimethyl ether hydrate³¹) until 1987, when Ripmeester et al. determined the Hexagonal structure H hydrate through X-ray powder diffraction and solid-state NMR studies.⁷

Calculation of clathrate hydrate properties, based on a statistical thermodynamical model were first made by Barrer and Stuart⁸ and by van der Waals and Platteeuw.⁹

Recent work¹² on clathrate hydrates includes studies of the thermodynamics and kinetics of hydrate formation, decomposition and inhibition of hydrate, molecular insights on hydrate formation, new developments in hydrate technology, discussions of hydrate distribution on the earth and their possible occurrence in the outer space,¹³ and the effects on the gas industry.

1.2 Fundamental Structure of Clathrate Hydrates

1.2.1 Structure Types

The general formula representing the formation of many clathrate hydrates is given by the following expression:

where M is the hydrate-forming molecule and n is the number of water molecules per gas molecule required to form a gas hydrate. The hydrogen-bonded water molecules comprise a “host” lattice around one or more species of “guest” molecules. The interaction between guest and host lattice is only through weak, non-specific van der Waals’ forces.

Clathrate hydrate structures are determined by the largest guest molecule present in the lattice. There are three structure types for which a large number of guests have been identified: the well-known classical cubic structures I (sI) and II (sII),^{10,11,14} and the more recently discovered hexagonal structure H (sH) hydrate.⁷

Each structure type can be characterized by the number and type of cages present which determine the ideal stoichiometry of the hydrate structure formed (**Figure 1-1**). Figure 1-1 shows the types of cages involved in the three main structures, and gives the crystal space groups, lattice parameters and the formulae describing the composition of the unit cells. All three structures have the ubiquitous pentagonal dodecahedral ($D-5^{12}$) small cage, although the symmetry of the cage is different for each structure. Structure H also contains a different small cage ($D' - 4^35^66^3$) of roughly similar size. In addition, the 14-hedron ($T - 6^25^{12}$), the 16-hedron ($H - 6^45^{12}$) and 20-hedron ($E - 6^85^{12}$) are the cages which contain the structure-directing guests for structure I, II and H respectively. The large cages increase in size progressively from structure I--> II--> H. The small cage of structure I and the large cage of structure II have cubic symmetry and are thus pseudo-spherical, whereas all the other cages can be described as oblate or prolate spheroids (possessing one unique axis). These cage symmetries have important consequences with respect to the motions and NMR properties of guest species. On the other hand, the

structure	small cage (radius Å)	large cage (radius Å)	unit cell formula	space group lattice parameter Å
sI	(D) 5^{12} (3.91)	(T) $5^{12}6^2$ (4.33)	$D_2T_6 \bullet 46H_2O$	$Pm3n$ $a=12.0$
sII	(D) 5^{12} (3.90)	(H) $5^{12}6^4$ (5.86)	$D_{16}H_8 \bullet 136H_2O$	$Fd3m$ $a=17.3$
sH	5^{12} (3.90) (D)	$4^35^66^3$ (3.85) (D')	$5^{12}6^8$ (8.31) (E)	$D_3D'_2E_1 \bullet 34H_2O$ $P6/mmm$ $a=12.2$ $c=10.1$

Figure 1-1 Three families of clathrate hydrate structures

stacking of the cage types which actually defines the crystal lattices is quite different for the three hydrate structures (**Figure 1-2**). Structure I hydrate is defined by specifying the vertices of the T cages, whereas structure II and H are based on different stacking sequences of layers of D cages connected by hydrogen bond bridges. Therefore, all the three structures give quite different X-ray diffraction patterns.

1.2.2 Guest Size - Structure Relationships

To form the clathrate hydrates, the guest species must be of suitable size and shape to enter the cavities which are formed by the hydrogen-bonded water framework. The type of hydrate structure that is formed depends primarily on the size of the hydrate forming molecule.

The guest size-hydrate structure relationship is shown in **Figure 1-3** which shows that hydrate structural transitions occur as the largest van der Waals' diameter (d) of the guest molecules increases, along with hydration numbers for some typical guest molecules. The smallest guests ($0.38\text{nm} < d < 0.42\text{nm}$), such as O_2 , N_2 , Ar, and Kr form structure II hydrate, with guests occupying both cages. CO is somewhat anomalous, as it forms structure I hydrate¹⁶, although it is of a similar size and isoelectronic with N_2 . Molecules such as H_2S , CH_4 , Xe ($d > 0.42\text{nm}$) form structure I hydrates with all the large cages and most of the small cages occupied. With increasing size ($0.42\text{nm} < d < 0.58\text{nm}$), the occupancy of the D cage drops, until for molecules like ethane and cyclopropane ($d = 0.58\text{nm}$) only the T cages are filled. A few molecules such as cyclopropane, trimethylene

Figure 1-2 Clathrate hydrate structures and stacking sequences of the cages: (a) structure I hydrate, projection along (100); (b) projection perpendicular to layer of D cages as in structure II and H hydrate; (c) projection along D cage layer, structure II; (d) projection along D cage layer, structure H (Ref. 29)

oxide or ethylene sulfide will form either structure I or II, depending on formation conditions. Larger molecules ($0.58\text{nm} < d < 0.70\text{nm}$) fill exclusively the large H cage of structure II hydrate. At the upper size limit for structure II hydrate, occupancy of the D cage by a small ('help gas') molecule can impart extra stability to the lattice so that larger molecules such as benzene, butane and cyclohexane ($0.70\text{nm} < d < 0.72\text{nm}$) still give stable hydrates, known as double hydrates. For still larger guest molecules ($0.72\text{nm} < d < 0.86\text{nm}$), structure H hydrate becomes the stable structure. Many substituted linear and cyclic hydrocarbons, including saturates, olefins and cage compounds such as adamantane are suitable guests for the large E cage. So far, the structure has only been made as a double hydrate, with small "help-gas" molecules occupying both the D and D' cages. A summary of hydrocarbon and related guests positively identified as hydrate formers is shown in **Table1-1**. Considering the size range and the diversity of chemical functionalities, the structure H hydrate family should be larger than the structure I and II families.

1.3 Thermodynamic and Structural Properties

A clathrate hydrate is a distinct phase in a multicomponent system. It is nonstoichiometric since, although the number of cages is fixed, their fractional occupancy is a function of temperature, pressure, and relative abundance of the species. Although the clathrate structure is different from that of other ice phases because of its large open structure, the water lattice is held together by the usual hydrogen bonding.¹⁵ The guest molecule-cage interaction is primarily the sum of core overlap effects (a strongly repulsive term) and an attractive van der Waals-like (induced dipole-induced dipole) interaction.

Figure 1-3 Guest size-hydrate structure relationship and hydration numbers (Ref. 29)

Table 1-1 Some potential gas hydrate formers in natural and industrial environments (Ref. 29)

Alkane	Alkenes, Alkynes, Aromatics
methane (I)	ethylene (I)
ethane (I)	propylene (II)
propane (II)	isobutylene (II)
isobutane (II)	allene (II)
butane (II)*	cis-2-butene (II)*
neopentane (II)*	2,3 dimethyl-2-butene (H)*
2 methylbutane (H)*	2,3 dimethyl-1-butene (H)*
2,2 dimethylbutane (H)*	3,3 dimethyl-2-butene (H)*
2,3 dimethylbutane (H)*	acetylene (I)
2,2,3 trimethylbutane (H)*	methylacetylene (II)
hexamethylethane (H)*	3,3 dimethyl-2-butyne (H)*
2,2 dimethylpentane (H)*	benzene (II)*
3,3 dimethylpentane (H)*	
Cycloalkanes, Cycloalkenes	Inorganics
cyclopropane (I,II)	O ₂ (II)
cyclobutane (II)	N ₂ (II)
cyclopentane (II)	H ₂ S (I)
cyclohexane (II)	CO ₂ (I)
methylcyclopropane (II)	SO ₂ (I)
methylcyclopentane (H)*	Cl ₂ (I)
methylcyclohexane (H)*	CFC's
cis-1,2 dimethylcyclohexane (H)*	
cyclooctane (H)*	
cyclopentene (II)	
cis cyclooctene (H)*	

I, II, H refer to structure types, starred entries require a help gas for stability

The included guest molecule must stabilize the cage structure because of the attractive term, since the empty cage structure is energetically unfavorable relative to the usual (more compact) forms of water ice.

1.3.1 Hydrate Phase Equilibria

Equilibrium thermodynamics are used to determine the conditions at which hydrates form or dissociate. The binary phase diagram of propane-water¹⁷ (Figure 1-4) is qualitative but illustrates the basic concepts for understanding both binary and multicomponent systems.

Figure 1-4. Temperature-composition diagram for the propane / water system (Ref. 17)

Most hydrate phase equilibrium measurements have been done under the three phase (liquid water-vapor-hydrate) condition similar to line L1. By the Gibbs Phase Rule, for a given pressure and a given dry hydrocarbon vapor composition (e.g. propane), the temperature of equilibrium of the three phases is determined. If a gas in equilibrium with its hydrate are heated at constant pressure, liquid water (with a slight amount of gas dissolved) will form at line L1, which is called the gas-liquid-hydrate line, the three phase line, or the dissociation curve. Conversely, cooling a gas-liquid mixture will result in hydrate formation at the three phase line. For multicomponent systems the position of line L1 is a strong function of gas composition. If an inhibitor such as methanol is added to the system, the L1 line will shift downward.

1.3.2 Thermodynamic Description of The Hydrate Phases

The basic theory for the prediction of hydrate equilibrium was derived by van der Waals and Platteeuw⁹ combining statistical thermodynamics with classical adsorption theory. The stability of the hydrate phase depends on the occupancy of the cages which constitute the hydrate lattice. If the guest molecule occupied only a small fraction of the hydrate cages, the hydrate lattice would not be stable and it would dissociate. The chemical potential of water in the hydrate phase is used as a measure of the stability of the hydrate structure.

If we consider the chemical potential of water in the hypothetical empty hydrate lattice as $\mu_w(h^0)$ and in the occupied hydrate as $\mu_w(h)$, then the difference between these two chemical potentials can be stated as,

$$\Delta \mu_w(h) = \mu_w(h^0) - \mu_w(h) \quad (1-1)$$

This difference in the chemical potential represents the decrease in the chemical potential of water as a result of the occupation of a hydrate cage by the guest molecule and was derived by van der Waals and Platteeuw as,

$$\mu_w(h^0) - \mu_w(h) = -RT \sum_m v_m \ln (1 - \sum_j \theta_{jm}) \quad (1-2)$$

where R is the gas constant, T is the absolute temperature, v_m is the number of cavities of type m per water molecule in the unit cell, and θ_{jm} is the occupancy of cavity m by component j , defined by,

$$\theta_{jm} = \frac{C_{jm} f_j}{1 + \sum_j C_{jm} f_j} \quad (1-3)$$

where f_j is the fugacity of the gas component j in the hydrate phase. At equilibrium it is equal to that of the same component in any other coexisting phase. C_{jm} is a Langmuir type constant for a guest molecule j in a type m cavity which depends only on temperature according to the relation,

$$C_{jm}(T) = \frac{4\pi}{kT} \int_0^\infty \exp \left[-\frac{w(r)}{kT} \right] r^2 dr \quad (1-4)$$

where k is Boltzmann's constant and $w(r)$ is the spherical symmetric cell potential and r is the radial distance from center of the cavity. The Langmuir constant describes the guest-water interactions inside the cage.

For constant temperature, eq. (1-3) becomes the Langmuir isotherm,

$$\theta_{jm} = \frac{KP_j}{(1 + KP_j)} \quad (1-5)$$

in which P_j is the decomposition pressure of the hydrate and K is a constant. By measuring the θ , one can then predict the decomposition pressure of hydrate.

When the hydrate is in equilibrium with ice, then $\mu_w(h) = \mu_w(\text{ice})$, and we can define $\Delta\mu_w^0 = \mu_w(h^0) - \mu_w(\text{ice})$; now $\Delta\mu_w^0$ represents the chemical potential of the empty lattice relative to ice, and eq (1-2) becomes,

$$\Delta\mu_w^0 = -RT \sum_m v_m \ln (1 - \sum_j \theta_{jm}) \quad (1-6)$$

For the structure I hydrate, since the stoichiometric ratio between guest and water is 6L:2S:46H₂O, eq (1-6) can be rewritten as,

$$\Delta\mu_{wI}^0 = - \frac{RT}{46} [6 \ln (1 - \theta_L) + 2 \ln (1 - \theta_S)] \quad (1-7)$$

where θ_L is the occupancy for "large" cavities in structure I and θ_S is the occupancy of "small" cavities.

By rewriting eq (1-7), one can then find θ_S in terms of θ_L ,

$$\theta_S = [1 - \exp (-23 \Delta\mu_{wI}^0 / RT)] / (1 - \theta_L)^3 \quad (1-8)$$

From values of θ_S , θ_L , and hence θ_S / θ_L , one can calculate hydration number,

$$n = 46 / (6 \theta_L + 2 \theta_S) \quad (1-9)$$

Since solid-state NMR is sensitive to the physical environments of the molecule (refer to chapter II), the guest in the small and large cages can be distinguished. From the observed NMR intensities, relative cage occupancy ratios θ_S / θ_L can be obtained and hence the hydration number.^{32,33,34,35} This therefore provides a non-destructive method of estimating the composition of structure I hydrates. The same principle can be used for structure II and structure H hydrates. **Table 1-2** is the summary of the θ_S / θ_L values for

structure I hydrates determined by the NMR experiments and Figure 1-5 gives the corresponding hydration number derived from the relationship to θ_s / θ_L .

**Table 1-2 Summary of NMR Measurement of Guest Molecule Cage
Occupancy Ratio and Corresponding Hydration Numbers for Structure I
Hydrates (Ref. 34)**

Structure I [*]	T(K) of NMR		Hydration	
Hydrate Guest	NMR	Measurement	θ_s / θ_L	Number (n)
CD ₃ F/D ₂ O	¹⁹ F(MAS)	243	~0.608	6.49
CD ₃ F/D ₂ O	² H	269	~0.525	6.63
CD ₃ CL	² H	243	0.268	7.14
D ₂ S/D ₂ O	² H	260	0.850	6.12
H ₂ Se	⁷⁷ Se	240	0.729	6.29
	⁷⁷ Se	275	0.780	6.21
D ₂ Se/D ₂ O	² H	230	0.753	6.25
	² H	270	0.775	6.22
C ₂ D ₂	² H	270	0.423	6.83
C ₂ D ₄	² H	273	0.212	7.26
CH ₄	¹³ C(CP/MAS)	193	0.916	6.04
CO	¹³ C (CP)	220	1.110	6.22
PH ₃	³¹ P (MAS)	201	0.474	6.73
Xe	¹²⁹ Xe (CP)	77	0.730	6.29

^{*} H₂O hydrate except where indicated

Figure 1-5 Variation of θ_s / θ_L versus hydration number n for structure I hydrate (Ref. 34)

1.4 Natural Occurrence of Gas Hydrate

1.4.1 Occurrence

The first existence of a naturally-occurring clathrate hydrate (aside from the natural gas pipeline), "air hydrate", was proposed by Miller¹⁸ to account for the presence of air found³⁹ in Antarctic ice cores taken at depths greater than 1200m. The discovery of large field of natural gas (CH_4) hydrate in Siberia¹⁹ occurred at about the same time as the discovery in oceanic sediments.²⁰ Similar natural gas hydrate fields have been found in Alaska and Northern Canada.^{21,22}

Many of the geological research activities focused on the mapping and characterization of geological deposits existing within the hydrate stable zone (HSZ). The importance of these studies was to determine the factors that permit or prohibit the formation of gas hydrates in the natural environment, both onshore and offshore.

Onshore Gas Hydrate: The cold surface temperatures in polar regions promote the occurrence of permafrost, and the resulting cold temperatures at depth lead to appropriate pressure/temperature conditions for gas hydrate formation. The first confirmation that gas hydrates occur onshore under permafrost was obtained in 1972 in the Prudhoe Bay field through cores from the North Eileen Well.

Gas hydrate is known to be present at the gas field of the western Siberian platform²³ and is believed to occur in other permafrost areas of northern Russia.²⁴ Permafrost-associated gas hydrate is also present in the North American Arctic.²⁵

Offshore Gas Hydrate: It has been recognized since the early 1970's that marine sediments may contain hydrates of natural gas.³⁶ This speculation was confirmed by Yefremova and Zhizhchenko³⁷ in samples from the Black sea. Later, gas hydrates were found in continental margin sediment on the landward wall of the Mid-America Trench.³⁸ The gases associated with most marine gas hydrates sampled thus far are methane-rich, that is, methane constitutes more than 99.9 percent of the hydrocarbon gases present.

Gas hydrates exist in marine sediments where the hydrostatic pressure exerted by the overlying water column is sufficient for hydrate formation. The necessary pressure generally restricts gas hydrates to sediments beneath water at least 300 to 600m deep. Higher sediment temperatures at greater sub-bottom depths destabilize gas hydrate;

therefore, hydrates are generally found only in the upper 300 to 1000m of marine sediments. Adequate temperature and pressure conditions for gas hydrate formation occur in shallow sediments of continental slopes and rises, as well as in the abyssal plains of all the world's oceans.

Only very recently, sH hydrate was first observed at 540 m water depth on the Gulf of Mexico continental slope.⁴⁰ In an earlier report, it was found that sII hydrate also occurs at similar water depths and temperatures in this area of the Gulf slope.⁴¹

1.4.2 Current Problems :

Industry: Practical interest in gas hydrates was generated initially in the natural gas industry when it was discovered that plugging of natural gas transmission lines was caused by hydrate formation.³ Since it is important to the natural gas industry to be able to know under what conditions hydrates will form, many studies⁴² were conducted to define the conditions for hydrate formation with compounds commonly found in natural gas.

Potential Energy Resource: In the 1950s and 1960s, unusual drilling experiences in arctic and offshore operations led to the speculation that hydrate could exist in nature and represent a potential gas resource. This speculation resulted in studies developed to evaluate the gas resource.

Gas hydrate will only become a potential energy resource if it can be shown that the cost of the energy required to release methane from the hydrate is significantly less than the economic value of methane that can be recovered from the dissociated gas hydrate deposits. The amount of methane present in gas hydrate is thought to be very

large. Such a large amount of methane, if commercially produced, could provide a potential energy resource for the future.

Environmental Concern: Because formation and decomposition of gas hydrate is sensitive to pressure and temperature, changes of surface pressure and temperature affect its stability. Destabilized gas hydrate beneath the sea floor may lead to geologic hazards such as submarine mass movements. The decomposition of gas hydrate may also have an effect on climate. The release of methane, a "greenhouse" gas, from destabilized gas hydrate may further enhance the global warming and be a factor in global climate change. Drilling and production of oil in deep ocean waters might be a cause for marine pollution due to gas hydrate formation.

Chemical injection has been one of the most straightforward way of preventing the formation of gas hydrates in the gas pipelines. However, the use of inhibitors like methanol and glycols is considered dangerous for the environment with the disposal of water containing those inhibitors.

1.5 Research Towards to Kinetics of Clathrate Hydrates

1.5.1 The Mechanism of Hydrate Formation

Recently, clathrate hydrate research is turning away from thermodynamic studies towards kinetic studies in order to understand hydrate formation and decomposition kinetics.

The process of clathrate hydrate formation has many similarities with that of crystallization. The process can be divided into nucleation and growth. The nucleation

process leads to the formation of critically sized, stable hydrate nuclei. The growth process commences immediately after the formation of stable nuclei. The formed particles grow due to the deposition of the gas in the hydrate phase during this process.

There are many hypotheses of hydrate formation. The hypothesis of formation of hydrate suggested by Christiansen and Sloan ²⁶ is briefly described as follows: When an apolar gas molecule dissolves in water, the water molecules around the apolar molecule become organized into a 'labile cluster'. The number of water molecules that participate in these labile clusters depends on the size of the gas molecule. It is postulated that these labile clusters play an essential role in the way hydrates form. These labile clusters may join together to form large agglomerates and, finally, the stable nuclei, and start to grow to form hydrate.

Figure 1-6 Overview of hydrate formation hypothesis (Ref. 26)

Figure (1-6) is a visual model of the hydrate formation, depicts the progress of molecular species from water (A) through labile clusters (B) to metastable agglomerates (C) to stable nuclei (D) at the end of the primary nucleation period and the start of growth.

1.5.2 Experiments Towards to Kinetics Studies

Experiments to study kinetic phenomena can be designed in several different ways. If the kinetic processes themselves cause dynamic effects on a time scale where changes in spectral appearance result, or where relaxation is affected, very little needs to be done except to study the temperature dependence and to extract rates for these processes. A second approach is to generate unstable or metastable states so that the approach to equilibrium can be followed, again by following changes in spectral appearance or relaxation phenomena.

Solid-state reactions in intimate mixtures of water and guest produced by vapor co-deposition at low temperature have been studied by NMR spectroscopic and X-ray powder diffraction techniques in order to understand some of the phenomena related to nucleation and kinetics. Devlin et al. have studied vapor-deposited thin films by means of vibrational spectroscopy,²⁷ and Hallbrucker and Mayer have used X-ray powder diffraction and calorimetry to follow hydrate formation in deposits of amorphous or cubic ice exposed to O₂, N₂, Ar, or CO at 1 atm.²⁸ Ripmeester et al. have extensively used NMR spectroscopic techniques, particularly ¹²⁹Xe NMR to study the local order of clathrate hydrate.²⁹ The use of NMR and X-ray powder diffraction measurements together allows

an assessment of both the short-range and long-range order in the clathrate hydrate, as discussed in Chapter II.

Current clathrate hydrate kinetic research is focused on the following areas:

- a. Primary nucleation, in which sub-critically sized crystals may grow or shrink before obtaining critical size,
- b. Crystal growth, in which growth occurs monotonically from nuclei that have already achieved critical size, and
- c. Kinetic inhibition of clathrate hydrate.

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Chapter II

Experimental Methods for Identification and Characterization of Clathrate Hydrates

The earliest techniques for identification and characterization of the clathrate hydrates involved diffraction experiments on powdered and single crystal hydrates, done most prominently by Von Stackelberg and coworkers,^{1,2} Jeffrey and coworkers,³ and more recently by Davidson, Ripmeester, and coworkers.^{4,5}

Very recently, spectroscopy has been used to determine different microscopic aspects of hydrates. Importantly, NMR spectroscopy has been used to detect and measure the occupation of different cages, dynamic characteristics of hydrates, and structural information.^{7,8}

2.1 X-ray Powder Diffraction^{6, 26}

2.1.1. The General Features of Crystals

Crystal Lattices and Unit Cells: A crystal is an orderly array of particles, and they are arrayed “symmetrically”. The particle is called asymmetric unit. The “space lattice” is a three dimensional, infinite array of points, which portrays the translational periodicity of the structure, hence is termed translation lattice. There are only fourteen distinct space lattices, referable to seven coordinate systems.⁶ The “unit cell” is the

fundamental unit from which the entire crystal may be constructed by purely translational displacements. The unit cell must possess the overall symmetry of the crystal.

Miller Indices: In three dimensions (with three axis a , b and c) a plane may always be found, parallel to a crystal face, which makes intercepts a/h , b/k and c/l on the unit cell edges, where h , k , l are three integers and referred to as the Miller indices. Miller indices are related to a particular unit cell and are therefore not uniquely defined for a given crystal face.

Spacing of Lattice Planes: The perpendicular distance between the individuals of a stack of lattice planes is known as the spacing of the planes and is denoted by the letter 'd'. The value of the interplanar spacing d_{hkl} depends on the dimensions of the unit cell, for example, the cubic system,

$$d_{hkl} = \left[\frac{1}{a^2} (h^2 + k^2 + l^2) \right]^{-1/2}.$$

2.1.2 Symmetry and Crystal Systems

Symmetry: A body is said to be symmetrical if it can be divided into exactly similar parts that can be brought into coincidence by some movement other than mere translation. Only three types of symmetry are possible, inversion through a point, reflection across a plane and rotation about an axis. A point of inversion, or center of symmetry, is present when for each face of the crystal there is a parallel, congruent face equidistant from, but on the opposite side of this point. A reflection or symmetry plane divides the crystal into halves which, by reflection across the plane, are mirror images of each other. Finally, a rotation or symmetry axis brings each face of the crystal into coincidence with a

similar, but not necessarily parallel face by a rotation of $2\pi/n$ about an axis; such an axis is designated n-fold.

Symmetry elements can be combined in groups and it can be shown that 230 distinctive arrangements are possible.⁶ Each of these arrangement is called a space group.

Crystal System: There are seven three-dimensional coordinate systems²⁶ which are useful in describing crystals and which are the basis for their classification.

Table 2-1 The crystal system with the unit cell parameter and space group (Ref. 26)

System	Type	Nature of Edges and Angles	Symmetry
Triclinic	P	$a \neq b \neq c; \alpha \neq \beta \neq \gamma$	1
Monoclinic	P	$a \neq b \neq c; \alpha = \gamma = 90^\circ \neq \beta$	2/m
	C	(b = twofold axis)	
	P B	$a \neq b \neq c; \alpha = \beta = 90^\circ \neq \gamma$ (c = twofold axis)	
Orthorhombic	P C (or A, B)	$a \neq b \neq c; \alpha = \beta = \gamma = 90^\circ$	mmm
	I		
	F		
Tetragonal	P I	$a_1 = a_2 \neq c; \alpha = \beta = \gamma = 90^\circ$	4/mmm
Trigonal	R	$a_1 = a_2 = a_3; \alpha = \beta = \gamma < 120^\circ \neq 90^\circ$	3/m
Hexagonal	P	$a_1 = a_2 \neq c; \alpha = \beta = 90^\circ; \gamma = 120^\circ$	6/mmm
Cubic	P	$a_1 = a_2 = a_3; \alpha = \beta = \gamma = 90^\circ$	m3m
	I		
	F		

In **Table 2-1** the crystal systems are listed with the unit cell parameters that characterize each. The characteristic symmetry of the cubic system is related to that of the rhombohedral, as may be seen in terms of a cube. Each body diagonal in a cube is a 3-fold axis. The designation of the cubic system is $m\bar{3}m$. The designation $6/mmm$ for the hexagonal lattice is the counterpart of that for the tetragonal lattice. The c axis in this system is a 6-fold axis with a mirror plane perpendicular to it. Parallel to the axis are two mutually perpendicular planes intersecting in a line coincident with c . The 6-fold axis generates additional mirror planes at 30° to those shown.

2.1.3. X-ray Diffraction

A crystal is a complex, although orderly, arrangement of atoms. All atoms in the path of an X-ray beam scatter X-rays simultaneously. In general, the scattered waves interfere with and destroy one another, but in certain specific directions they combine to form new wave fronts. This cooperative scattering is known as diffraction. The directions of possible diffraction depend only on the size and shape of the unit cell. Certain classes of diffraction are systematically extinguished by lattice centering and by the presence of space-group symmetry elements. The intensities of the diffracted waves depend on the kind and arrangement of atoms in the crystal structure. Thus a study of the geometry of diffraction from a crystal yields the unit cell dimensions. An analysis of the missing diffraction spots gives the symmetry (space group) of the crystal structure. The intensities are needed to work out the arrangement of atoms.

The Condition For Reflection: The condition for reflection was theoretically described by the well known Bragg's law ¹⁰.

Figure 2-1 shows a beam of parallel X-rays penetrating a stack of planes of spacing d , at a glancing angle of incidence θ . Each plane must be pictured as reflecting a fraction of the incident beam. The reflected rays combine to form a diffracted beam if they differ in phase by a whole number of wavelengths, that is, if the path difference $AB - AD = n\lambda$, where n is 1,2,3, etc.

$$AB = d / \sin\theta,$$

$$AD = AB \cos 2\theta = d (\cos 2\theta) / \sin\theta,$$

$$\text{therefore, } n\lambda = d / \sin\theta - d(\cos 2\theta)/\sin\theta = d(1 - \cos 2\theta)/\sin\theta = d(2\sin^2\theta)/\sin\theta,$$

$$\text{that is } n\lambda = 2d\sin\theta.$$

This is the Bragg condition for reflection.

The Bragg equation gives the angle θ , at which a set of planes of spacing d cooperatively reflects X-radiation of wavelength λ in the n th order.

Figure 2-1 The condition for reflection - the Bragg law (Ref. 6)

The Powder Diffraction Method: The powder method derives its name from the use of a polycrystalline sample which may take many physical forms but is usually a powder. Ideally, all possible orientations of all possible lattice planes are present in a powder sample, and when a beam of characteristic radiation is directed at the sample the Bragg condition for the reflection is simultaneously satisfied for all types of lattice plane.

The principle of the powder method is illustrated by the diagrams of **Figure 2-2**. **Figure 2-2a** shows a particular set of lattice planes in one crystallite oriented at the appropriate Bragg angle θ to the incident beam. The reflected beam makes an angle 2θ (the diffraction angle) with the undeviated beam. The figure depicts only one of an infinite number of ways in which this, or an identical set of planes in another crystallite, can be oriented at the same angle θ to the beam. The reflected beams which correspond to these orientations outline a cone, which is coaxial with the incident beam and has a half-apex angle 2θ (**Fig. 2-2b**). Simultaneously, other lattice planes with different spacings satisfy the Bragg condition and generate reflection cones, which are also coaxial with the beam but have different half-apex angles (**Fig. 2-2c**). To ensure the existence of cones, it is usually necessary to rotate, oscillate, or otherwise move very small samples continuously during the exposure. Reflections developed at 2θ angles of less than 90° are described as front or forward reflections and at angles greater than 90° as back reflections. These reflections are recorded by an X-ray detector.

The characteristic features of an X-ray powder spectrum are the angles at which reflections occur and the relative intensities of the reflections. The reflection angles θ depend on the wavelength λ and the interplanar spacings d_{hkl} in accordance with the Bragg

law $\lambda = 2d_{hkl} \sin \theta$. The spacings in turn depend on the dimensions of the unit cell. The relative intensities of the reflections depend on the kind of atoms and their arrangement between the lattice planes. A powder spectrum is therefore a reasonably complete display of the diffraction effects from a compound.

Figure 2-2 The principle of powder method (Ref. 6)

The Interpretation of X-ray Powder Data: The procedure in analyzing the powder spectrum of an unknown compound consists of measuring the diffraction angles, calculating the spacings of the reflecting planes, and then deducing the dimensions of the unit cell.

One procedure for indexing the reflection of a powder pattern when the crystal system and unit cell dimensions are known is to calculate all d values for the cell with the aid of the appropriate spacing formula. A comparison of measured and calculated spacing gives the indices of the reflections.

When only the crystal system is known, the process of indexing is essentially one of deriving a unit cell, the calculated spacing of which are in agreement with the measured spacings.

The program for interpretation of X-ray powder diffraction data, called 'TREOR', was written by Werner.^{27,28,29,30} This is a general TRial-and-ErrOR indexing program for X-ray diffraction powder patterns. Typically, an integrative program 'fits' observed 2θ or d values and generates possible space groups and unit cells, then enters new calculated 2θ or d values until spectrum is fitted.

2.1.4 Profile for Three Different Hydrate Structures

X-ray diffraction techniques have been widely used to identify the crystal lattice of hydrate structures.¹⁻⁵ The detailed single-crystal structure analyses have already been reported for structure I²² and for structure II²³, although the recently discovered structure H still lacks single crystal data. Values at 0°C of the lattice parameter of the structure I unit cell lie between about 11.97 and 12.15 Å, while that of structure II is 17.14 to 17.57 Å. The exact value depends on the guest molecules present. For hexagonal structure H hydrate, the lattice parameters are given by $a = 12.00 \sim 12.26$ Å and $c = 10.00 \sim 10.17$ Å.

Many X-ray measurements have been made at low temperatures (110 to 170K), where the patterns are better defined and the hydrate stability is assured.¹¹

Table 2-2 Commonly observed spacings in X-ray (Co radiation 0.17892nm)

powder diffraction patterns of ice Ih and the hydrates

Structure I Hydrate Pm3n, a = 1.1907 nm		Structure II Hydrate Fd3m, a = 1.7111 nm		Structure H Hydrate P6/mmm, a = 1.226 c = 1.017 nm		Ice Ih P63/mmc, a = 0.452 c = 0.736 nm	
hkl	d	hkl	d	hkl	d	hkl	d
110	8.532	111	10.031	112	3.921	100	3.914
200	6.007	220	6.106	202	3.683	002	3.680
210	5.357	311	5.194	301	3.335	101	3.456
211	4.896	222	4.975	212	3.152	102	2.681
220	4.237	400	4.302	220	3.073	110	2.260
310	3.782	331	3.941	310	2.951		
222	3.457	422	3.507	221	2.924		
320	3.315	511	3.306	203	2.855		
321	3.196	440	3.035	411	2.260		
400	2.987	531	2.901				
410	2.895	600	2.862				
330	2.815	620	2.713				
421	2.604	533	2.625

Figure 2-3 X-ray powder diffraction patterns of ice Ih and three types of hydrates

(a) ice(h), (b) sI (Xenon), (c) sII (Pentafluoropropane), (d) sH (Neohexane / Xe)

The lattice symmetries of ice and the three hydrates are all distinct, and the lattice parameters of the individual structures vary only slightly with the nature of the guest molecule, so that the line positions in the powder diffraction patterns are completely diagnostic of the structure. Commonly observed spacings for the three hydrates structures and normal hexagonal ice are given in **Table 2-2**. **Figure 2-3** shows distinct X-ray powder diffraction patterns for ice(h), sI (Xenon), sII (Pentafluoropropane) and sH (Neohexane/Xenon) hydrate, respectively.

A weak point of the technique is that the powder diffraction patterns of mixtures are more difficult to deal with.

2.2 Nuclear Magnetic Resonance (NMR) Spectroscopy

2.2.1 Basic Principles⁹

When a nucleus with magnetic moment μ is placed in an external magnetic field B , the interaction energy of μ and B in quantum theory, the Hamiltonian H , is given by $-\mu \cdot B$. Furthermore, since the dimensionless spin operator I is defined by $\mu = \gamma \hbar I$, we have,

$$H = -\mu \cdot B = -\gamma \hbar I \cdot B \quad (2-1)$$

where γ is the gyromagnetic ratio, and $\hbar$ is Planck's constant divided by 2π .

The interaction energy of the spin and the external magnetic field that is given by eq.(2-1) is generally called the Zeeman energy, H_z .

Now, when the external magnetic field is a static field B_0 along the Z axis, eq.(2-1) reduces to

$$H = -\gamma \hbar B_0 I_z \quad (2-2)$$

Therefore, the eigenstates of energy are the same as those of I_z and they are $-\gamma\hbar B_0$ times the eigenvalues of I_z . That is, the E_m values take one of $(2I + 1)$ values

$$E_m = -\gamma\hbar B_0 m \quad (m = I, I-1, \dots, -I) \quad (2-3)$$

The energy difference ΔE between neighboring energy levels becomes

$$\Delta E = \hbar \omega_0 \quad (2-4)$$

with $\omega_0 = -\gamma B_0 \quad (2-5)$

where ω_0 is called the Larmor frequency.

If a linearly oscillating field of frequency ω_0 is applied perpendicular to the static field, a state transition occurs between neighboring energy levels of the spin system and the so-called nuclear magnetic resonance phenomenon is observed.

2.2.2 Important NMR Interactions and Their Hamiltonians:¹²

The Zeeman interaction H_Z , as shown in eq.(2-1), is by far the strongest interaction and dominates the behavior of the nuclear spin system, but contains no relevant structural information itself. In addition, the Hamiltonian of a spin system consists of a number of lower energy interactions that can be detected by NMR spectroscopy. Hence, the total Hamiltonian of the spin system, H_T , consists of the Zeeman energy H_Z and the internal Hamiltonian H_I ,

$$H_T = H_Z + H_I \quad (2-6)$$

where H_I has many terms of interest,

$$H_I = H_{CS} + H_J + H_D + H_Q \quad (2-7)$$

These low energy contributions to the Hamiltonian, which can be termed 'local field', give rise to the linewidth, shifts and satellites to the zero order absorption lines caused by H_z . These terms provide important information about the electronic environment around nuclei and the spatial alignment of nuclei and can be calculated in terms of (time-independent) first-order perturbation theory.¹⁸

Chemical Shift Interaction: The chemical shift is an indirect interaction between the spins and the external field B_0 via electrons and the chemical shift Hamiltonian H_s can be expressed as,

$$H_s = \gamma \hbar I \sigma B_0 \quad (2-8)$$

where σ , the chemical shielding tensor, is a second rank tensor.

In the solid sample, because the electronic environment about a nucleus is not spherical, i.e. the distribution of electrons is anisotropic, the shielding tensor σ can be expressed by,

$$\sigma = \sigma_{11}\lambda_{11}^2 + \sigma_{22}\lambda_{22}^2 + \sigma_{33}\lambda_{33}^2 \quad (2-9)$$

The principal values (σ_{11} , σ_{22} , σ_{33}) give the magnitude of the tensor σ in three perpendicular directions, and the λ_s are direction cosines specifying the orientation of the molecular principal coordinate system with respect to the applied field B_0 . In solution, the rapid molecular motion results in the observation of their isotropic chemical shifts, σ_1 , obtained by averaging the chemical shift tensor σ over all orientations,

$$\sigma_1 = 1/3 (\sigma_{11} + \sigma_{22} + \sigma_{33}) = 1/3 \text{ trace } \sigma \quad (2-10)$$

Although the chemical shift interaction may not always be significant in the solid state, it is the dominant perturbing interaction in high-resolution NMR experiments.

Spin-Spin Coupling (Scalar-Coupling) Interaction: The spin-spin coupling is an indirect interaction between neighboring nuclear magnetic moments transmitted by electrons through intermediate bonds. The interaction Hamiltonian between a pair of spins i and j may be represented as,

$$H_J = \sum_{i,j} \mathbf{I}_i \cdot \mathbf{J} \cdot \mathbf{I}_j \quad (2-11)$$

Spin-spin (scalar) coupling contributes to fine structure of NMR signals. The magnitude of the splitting is termed the spin-spin coupling constant J and is usually of no consequence in solid-state NMR experiments on the lighter elements, for it is relatively small compared with other “local field” interactions in the solid sample.

The Dipolar Interaction: The dipolar interaction results from the dipole-dipole (through space) interaction between nuclei with spin. For two identical nuclei i and j , the dipolar interaction $H_{D(i,j)}$ may be written as,

$$H_{D(i,j)} = \gamma_i \gamma_j \hbar^2 / r_{ij}^3 (\mathbf{I} \cdot \mathbf{D}_{ij} \cdot \mathbf{J}) \quad (2-12)$$

where r_{ij} is the internuclear distance; γ_i, γ_j are the magnetogyric ratios; $\mathbf{I}, \mathbf{J}$ are the spin operators of the two nuclei respectively. The $\mathbf{D}_{ij}$ is the dipolar coupling tensor, its magnitude can be expressed as,

$$D_{ij} = \hbar \gamma_i \gamma_j / 8\pi^2 [(3\cos^2 \theta_{ij} - 1) / r_{ij}^3] \quad (2-13)$$

where θ_{ij} is the angle between the internuclear vector and the magnetic field B_0 .

Dipolar coupling is a dominant factor in determining the NMR spectrum of solids and anisotropic liquids; however, rapid molecular reorientation averages θ such that dipolar coupling is zero, and in mobile liquids and molecules in isotropic solution, dipolar coupling makes no contribution to the line positions in the NMR spectrum.

The Quadrupolar Interaction: The quadrupolar interaction H_Q occurs only for the nuclei with spin greater than $1/2$ (e.g. ^2H , ^{17}O , ^{27}Al). In these cases there is a non-symmetrical charge distribution within the nucleus creating an electric quadrupole moment, eQ , which interacts with electric field gradient (efg) around the nucleus,

$$H_Q = \frac{eQ}{6I(2I-1)} \mathbf{I} \cdot \mathbf{V} \cdot \mathbf{I}$$

$$= \frac{eQ}{6I(2I-1)} \sum_{\alpha\beta} V_{\alpha\beta} \left[\frac{2}{3} (I_\alpha I_\beta + I_\beta I_\alpha) - \delta_{\alpha\beta} I^2 \right] \quad (2-14)$$

where $V_{\alpha\beta}$ is the efg second tensor (α, β). The components of $\mathbf{V}$ describe completely the orientation and magnitude of the efg. When the effective quadrupole interaction of (2-14) applies for an arbitrary orientation of the rectangular coordinates $\alpha = x, y, z$. The tensor $V_{\alpha\beta}$ can be characterized by only three principal elements V_{xx} , V_{yy} and V_{zz} to give,

$$H_Q = \frac{eQ}{4I(2I-1)} [V_{zz} (3I_z^2 - I^2) + (V_{xx} - V_{yy})(I_x^2 - I_y^2)] \quad (2-15)$$

It is customary to define two symbols, η and q , called the asymmetry parameter and the field gradient, by the equations,

$$eq = V_{zz} \quad (2-16)$$

$$\eta = (V_{xx} - V_{yy}) / V_{zz} \quad (2-17)$$

The asymmetry parameter η measures the departure from cylindrical symmetry of the efg tensor. If the electric field gradient is symmetric about the principal axis, V_{zz} will be unique, $V_{xx} = V_{yy}$ and $\eta = 0$ and the interaction is said to be 'axially symmetric'.

2.2.3 Solid State Deuterium NMR

^2H NMR has been developed into an excellent probe of dynamic processes in the solid state for motions of frequency 10^3 - 10^7 Hz. Because of the comparable size of the quadrupolar coupling constant and the rates of motion, the ^2H NMR lineshapes can be affected by the dynamic processes.

The Characteristics of ^2H NMR Spectra:

For ^2H (Table 2-3), the quadrupolar interaction generated by the interaction of the nucleus with the magnetic field and the electric field gradient dominates other anisotropic interactions. Hence, the total Hamiltonian for the system is the sum of the Zeeman and quadrupolar Hamiltonian:

$$H_T = H_Z + H_Q \quad (2-18)$$

Table 2-3 Nuclear parameters of ^2H nuclei

Spin, I	1
% Natural Abundance	0.015
Quadrupole Moment($\times 10^{-31}$ Q/m ²)	2.8
Gyromagnetic Ratio ($\times 10^7$ rad s ⁻¹ T ⁻¹)	4.1
Frequency at (^1H =200MHz) (MHz)	30.702

The energy level diagram for the combined Zeeman and Quadrupolar interactions for a spin 1 nucleus is given in Figure 2-4a. There are two transition frequencies that result from the perturbation of the three Zeeman levels by quadrupolar interaction. The magnitude of this quadrupolar splitting is given by

$$\Delta\nu_q = 3 e^2 q Q / 2h \left[(3 \cos^2 \theta - 1) / 2 + \eta \sin^2 \theta \cos^2 \phi / 2 \right] \quad (2-19)$$

there, θ , ϕ are the angles relate efg. to external magnetic field B_0 direction. The collective term $(e^2 q Q / h)$ is known as the 'quadrupole coupling constant' and may be evaluated directly from NMR studies of the solid spectra.^{16,17} For deuterons attached to carbon, it has values between 170 and 200 kHz with the principal axis being the vector of the (C-D) bond.⁷

(a)

$$\Delta\nu_q = \frac{3}{4} \frac{e^2 q Q}{h} (3 \cos^2 \theta - 1)$$

(b)

Figure 2-4 Depiction of the energy levels of a nucleus, spin $I = 1$ (Ref.9)

When the cfg is axially symmetric (Figure 2-4b), the asymmetry parameter, η , is reduced to zero, the quadrupolar splitting is dependent upon one orientation angle, θ , which the V_{zz} makes with B_0 , and the eq.(2-19) becomes:

$$\Delta\nu_q = \frac{3}{4} \frac{e^2 q Q}{h} (3\cos^2\theta - 1) \quad (2-20)$$

In a powder sample all orientations exist and the resulting ^2H spectrum shown in Figure 2-5, has a particular shape and is known as a Pake powder pattern.

Figure 2-5 ^2H lineshapes for (a) $\eta=0$, (b) $\eta=0.2$, and (c) $\eta=1$ indicating the frequency separations $\Delta\nu_{xx}$, $\Delta\nu_{yy}$ and $\Delta\nu_{zz}$ (Ref. 20)

Three sets of features can be recognized in a typical ^2H powder pattern: outer steps, shoulders, and maxima, with characteristic splittings:

$$\Delta\nu_{zz} = 3e^2qQ/2h \quad (2-21)$$

$$\Delta\nu_{yy} = 3e^2qQ/4h (1+\eta) \quad (2-22)$$

$$\Delta\nu_{xx} = 3e^2qQ/4h (1-\eta) \quad (2-23)$$

hence, quadrupolar coupling constant χ and asymmetry parameter η can be measured from ^2H powder pattern, i.e.,

$$\chi = e^2qQ/h = 2/3 \Delta\nu_{zz} \quad (2-24)$$

$$\text{and} \quad \eta = (\Delta\nu_{xx} - \Delta\nu_{yy}) / \Delta\nu_{zz} \quad (2-25)$$

Effects of Motion on Lineshapes: An extremely important aspect of ^2H NMR is its lineshape information use in the study of molecular dynamics. In general, a molecule in a solid will undergo motion at increasingly rapid rates as temperature increases. Motion at a rate of $< 10^3 \text{ s}^{-1}$ has no effect on the ^2H NMR lineshapes and is said to be in the “slow” (rigid) motion limit. With the temperature increasing, motion at the intermediate rates (10^3 - 10^7 s^{-1}) gives rise to distorted ^2H NMR lineshapes in a manner that depends upon the angular extent, specific rate of motion and the experimental details (eg. echo delay time). When the fast motion limit (f.m.l.) is reached (above 10^7 s^{-1} rate) , changes in the lineshape are complete.

Fast motion limit: It is relatively easy to obtain analytical expressions for the line shapes in the f.m.l.¹⁹ The static efg tensor must first be described in a reference frame in terms of the Euler angles:

$$\mathbf{V}(\alpha, \beta, \gamma) = \mathbf{R} \mathbf{V}_{\text{pas}} \mathbf{R}^{-1} \quad (2-24)$$

where $\mathbf{R}$ is the Euler angle rotation matrix describing the coordinate transformation and $\mathbf{V}_{\text{pas}}$ is the tensor in its PAS (principal axis system). The complete description of the static tensor in the reference frame is

$$\mathbf{V}(\alpha, \beta, \gamma) = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} \quad (2-25)$$

where $a_{ij} = a_{ji}$, can be found elsewhere.²⁰

Intermediate Motion Linshapes: Between the fast-motion limit and the rigid limit we have an intermediate motional regime as caused by the molecular reorientation between different sites. For reorientation between two sites within one crystallite the situation is analogous to that for chemical exchange in solution. At any one rate of motion, the exchange averaging effects are at different stages for each crystallite orientation; some components will be broad, others narrow. Their sum constitutes the grossly distorted lineshape.

There are no analytical expressions for the distorted dynamically exchanging lineshapes. However, they can be simulated by numerical calculation,^{19,21,24} and these can then be used to determinate a jump rate (and hence a correlation time τ_c value) for a particular observed line shape at a certain temperature by comparison. This is then potentially a route of obtaining an Arrhenius plot and an activation energy for the motion.

Typical spectra are shown for a benzene molecule.⁷ **Figure 2-6a** shows the lineshape for benzene held rigidly in the lattice, **Figure 2-6b** where the fragment performs

rapid twofold flips about the C_1-C_4 axis, and Figure 2-6c where the fragment rotates about the same axis but now among three or more equivalent sites.

Figure 2-6 ^2H NMR lineshapes for Benzene hydrate (Ref. 7)

Computer Simulation of ^2H NMR Spectra: The variable ^2H NMR lineshapes were simulated according to a program written by Greenfield, et al²⁴. Input consists of the number of independent jumping sites, the Eulerian angles which specify the allowed orientations within each site, and rates of the simple processes definable within individual site. The program then generates look-up tables for calculating sites frequencies at each point of an orientational grid specified by means of a tiling scheme. Additional parameters required for calculation are the spectrometer parameters including the time τ_1 between the two pulses in a quadrupole-echo pulse sequence and also the amplitude and duration of the pulses. The program begins calculating the signal somewhat before the echo maximum, whose precise location after the second pulse depends not only on the pulse spacing τ_1 but also on the exchange rate, pulse widths, and pulse amplitude. The calculation includes contributions from virtual FID as well as the echo, and also corrections for imperfect spectral coverage by finite pulse and exchange during pulses. Output lineshapes for different input conditions may be normalized to a common maximum peak height for pulse of display. The normalized factors are preserved and reported, to facilitate comparison of lineshapes obtained with different pulse spacing and hence different echo attenuation factors.

2.3 Summary

X-ray diffraction techniques have played an important role through the long history of clathrate hydrate studies and provided detailed structural information.

On the other hand, clathrate hydrates are solids consisting of weakly interacting host and guest molecules, NMR spectroscopy which is sensitive to the considerable reorientational mobility of guest molecules has also become a more useful technique in clathrate hydrate studies, particularly in providing information about molecular motion, as well as other structural parameters of clathrate hydrates.¹¹ The list of nuclei which have now been used in NMR studies of clathrate hydrates includes ^1H , ^2H , ^{13}C , ^{19}F , ^{31}P , ^{77}Se , and ^{129}Xe .⁷

Specifically, ^{129}Xe NMR spectroscopy is a useful tool in the study of hydrate structure; although this is a highly specialized application,¹² it has proved to be efficient in the screening of hydrate formers,¹³ and in fact played a important role in the identification of structure H hydrate.¹⁴ From NMR measurements, both guest molecule cage occupancy ratio and corresponding hydration number can be determined. ^{13}C anisotropic lineshapes and the ^2H lineshapes can be used to study the molecular motion in the clathrate hydrates.^{7,15}

Finally, the important difference between NMR and diffraction techniques should be noted. Because diffraction techniques depend on lattice symmetry, and hence, long-range order, space averaging is inherent in this technique. On the other hand, NMR spectroscopy depends on short-range interactions. Both techniques are sensitive to molecular motion, although the scale for time averaging is quite different for the two methods. The use of NMR and X-ray powder diffraction measurements together allows an assessment of both the short-range and long-range order in the clathrate hydrate samples.

2.4 References

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Chapter III

Formaldehyde Clathrate Hydrate

3.1 Introduction

3.1.1 Formaldehyde in Space

Increasing interest in the occurrence of clathrate hydrates in the outer solar system and galaxy has arisen recently,¹ though this possibility has been recognized for at least 25 years.² Since extraterrestrial conditions are entirely different from those on earth, there is considerable scope for the existence of hydrates with unusual guest species. Clathrate hydrates with guests such as CO₂, CO, CH₄, O₂, N₂, have been suggested to occur in association with the icy environments of the outer planets and comets, and an analysis of the thermodynamics and kinetics of clathrate formation under conditions of interest to outer solar system studies have also been proposed.³ However there is no direct evidence for the existence of clathrates anywhere aside from Earth.

Formaldehyde is a molecule which has been associated with the extraterrestrial environment for a long time and is the third most abundant gaseous molecule after the H₂ and CO observed in the interstellar medium.⁴ Its linear polymer, polyoxymethylene (POM), was the first polymer to be identified in space, and is postulated to be the main component of interstellar dust.⁵ Wickramasinghe went so far as to discuss the formation of anhydrous as well as hydrated polymers from the polymerization of formaldehyde on dust grains, but did not consider clathrate hydrate formation.⁴ In a normal terrestrial

environment, gas hydrates form by direct contact between liquid water or water vapor and guest material at suitable temperatures and pressures.⁶ Under such conditions, formaldehyde hydrate cannot be expected to form, as formaldehyde in aqueous solution is hydrolyzed rapidly to give a geminal diol⁷ and hence it is deemed to be unsuitable as a guest for the clathrate hydrates. However, it has already been recognized that clathrate hydrates form quite readily either by annealing intimate mixtures of guest and water co-deposited at low temperatures,⁸ or by exposing highly porous amorphous solid water to low pressures of gases such as O₂, N₂, Kr and CO,^{9,10} and more recently, NO¹¹. It is entirely possible that deposition of formaldehyde gas along with water vapor at low temperatures may well allow a clathrate hydrate to form without interference from hydrolysis or polymerization. From the largest van der Waals' diameter of formaldehyde, 0.47nm, the molecule should be suitable as a guest for the structure I hydrate large cage, although there could be some occupancy of the small cage as well.

3.1.2 Chemistry of Formaldehyde⁷

Formaldehyde has a melting point of 181.2K and a boiling point of 252.2K. Its aqueous solution is called formalin. Although formaldehyde can be liquefied readily, it cannot be handled safely in this form because it polymerizes explosively even at temperatures just above its freezing point, and no effective stabilizers are known. Normally, formaldehyde can be transported and stored as the solid polymer known as paraformaldehyde, which is prepared by concentrating formalin at reduced pressure:

Paraformaldehyde is a linear, amorphous solid of high molecular weight that is insoluble in water. Anhydrous, gaseous formaldehyde can be prepared most conveniently by heating paraformaldehyde at a temperature above 120 °C.

Formaldehyde in aqueous solution does not display the sensitivity to air oxidation and general reactivity characteristic of the aldehyde in the gaseous state and hence is probably present to a considerable extent as the geminal diol.

Since the carbonyl group of formaldehyde has greater additive power than that of higher aldehydes, the equilibrium is probably particularly favorable to the gem-diol.

3.1.3 ^2H NMR Spectroscopic Methods

As we pointed out in Chapter II, deuterium has a spin = 1 nucleus whose NMR behavior in solids is normally dominated by the coupling between its quadrupole moment and the electric field gradient at the site of the nucleus. This interaction is larger than the dipolar coupling by more than an order of magnitude and very sensitive to molecular orientation. It disappears completely only in the presence of isotropic rotation (or its equivalent). Therefore, significant information about molecular motions can be contained in the ^2H NMR lineshape over the frequency of 10^3 - 10^7 Hz. The motion of formaldehyde- d_2 as a pure solid and in the clathrate cage should be very different, and hence it is expected the ^2H NMR will be a good technique to monitor the presence of clathrate.

^2H NMR lineshapes can be affected by dynamic processes. Information on the rate and mechanism of dynamic processes appears in several different ways in quadrupole echo spectra.²² For our instance, the temperature dependence of the ^2H line shapes may be studied. Variation of the temperature provides a means to adjust the rates of dynamic processes so they fall into the slow, intermediate, or fast limit regimes and therefore dramatically change the shape of the spectral lines.

3.2 Experimental Section

3.2.1 Sample Preparation

The formaldehyde hydrate precursor was prepared in a Pyrex glass vacuum line. Two flasks, one containing a known amount of paraformaldehyde powder (Fisher Chemical) and the other distilled water, were connected to the vacuum line and allowed to degas. Paraformaldehyde was then heated at about 110°C to generate formaldehyde vapor. This was co-deposited with water vapor on a cold finger cooled by liquid nitrogen. The co-deposition rate of the vapors was controlled by two valves, so that the mole ratio of formaldehyde to water was approximately 1 : 6. The deposit was then transferred to a Pyrex tube stored in liquid nitrogen, and ready for X-ray diffraction. For the ^2H NMR measurements, paraformaldehyde- d_2 (MSD Isotopes, 99.3 atom %D) was co-deposited with normal water or heavy water (MSD Isotopes, 99.9 atom %D). The deposit was transferred to a NMR tube (10mm) and sealed for NMR determination.

3.2.2 X-ray Powder Diffraction

Samples of the product were loaded into the variable temperature sample cell of a Rigaku θ - θ X-ray powder diffractometer. The sample was handled in liquid nitrogen in order to minimize water condensation and hydrate decomposition. X-ray powder diffraction patterns were recorded with $\text{CoK}\alpha$ ($\lambda = 0.17892\text{nm}$) radiation. For each sample, a diffraction pattern from $2\theta = 10^\circ$ - 60° was recorded. The scan speed was $0.5^\circ/\text{min}$ with an increment step size of 0.02° . The typical count rate on a peak was about 100-200 cps. The raw data were smoothed using a spline fitting procedure.¹⁹ The variable annealing temperatures were obtained with a Paar controller. Finally, the X-ray diffraction data were interpreted by the "TREOR" program (Ref. Chapter II) to obtain unit cell parameters.

3.2.3 ^2H NMR Spectroscopy

^2H NMR powder spectra were recorded on a Bruker MSL-200 spectrometer at 30.7MHz. The sample was sealed in a Pyrex tube (10mm) suitable for insertion into the solenoid coil of a low temperature NMR probe. The various temperatures were obtained by using a variable-temperature N_2 gas-flow probe with a Bruker B-VT-1000 temperature controller. The measurements at liquid nitrogen temperature were carried out using a probe designed to hold liquid nitrogen around the sample. A phase alternated quadrupole echo pulse sequence was used²⁰

$$[(\frac{\pi}{2})_x - \tau - (\frac{\pi}{2})_y - \tau - \text{acquire} - \text{delay}]_n$$

which consists of a pair of 90° pulses separated by a time τ . The echo occurs at a time τ after the second pulse. In our work, the echo delay time τ was $34\mu\text{s}$ and the 90° degree pulse length was $2\text{-}3\mu\text{s}$.

3.3 Results and Discussion

3.3.1 X-ray Powder Diffraction Patterns

X-ray powder diffraction results showed that at 90K most of the co-deposit of formaldehyde/water was amorphous, although a few reflections can be attributed to ice Ic (**Figure 3-1a**). Annealing at 150K showed that essentially all of the remaining amorphous material was converted to crystalline product (**Figure 3-1b**). Most (19 out of 23) of the reflections can be indexed in terms of a cubic structure I clathrate hydrate and a small quantity of ice Ic. The low angle reflections (110, 210, and 211) are especially diagnostic of the structure I lattice with its relatively large unit cell. A least squares fit to 14 reflections yielded a lattice constant of 1.1971nm (**Table 3.1**), well within the usual range of values observed for the structure I hydrate lattice.²¹ The powder diffraction pattern of formaldehyde hydrate also contained some reflections due to ice which can be differentiated from the overlapping hydrate pattern by comparing with the diffraction pattern measured after decomposing the hydrate sample. This can be done by annealing the sample in the open X-ray powder cell at temperatures above about 220K which converted much of the clathrate and ice Ic into ice Ih (**Figure 3-1c**).

Figure 3-1 X-ray powder diffraction pattern of a) a vapor deposit of water vapor and formaldehyde gas prepared from a paraformaldehyde precursor at 90K; b) after annealing at 150K; c) after annealing at 220K.

Table 3-1 X-ray diffraction powder pattern of formaldehyde clathrate hydrate listing experimental d spacings, and those calculated from the least squares fit which gives a lattice constant of 1.1972(3) nm for the structure I hydrate unit cell.

h	k	l	d_{obs}	d_{calc}
1	1	0	8.4570	8.4653
2	1	0	5.3692	5.3539
2	1	1	4.9038	4.8874
2	2	2	3.4662	3.4559
3	2	0	3.3179	3.3204
3	2	1	3.2052	3.1996
4	0	0	2.9928	2.9929
4	1	0	2.9079	2.9036
3	3	0	2.8190	2.8218
4	2	1	2.6128	2.6124
3	3	2	2.5524	2.5524
5	2	0	2.2227	2.2231
4	4	1	2.0865	2.0840
5	3	0	2.0530	2.0531

3.3.2 ²H NMR Results

a. Molecular Motion of the Formaldehyde Molecule

²H NMR powder lineshapes of pure formaldehyde-d₂ (D₂CO) were obtained as a function of temperature at 30.7MHz (Figure 3-2a). Below ~90K, the ²H NMR pattern is a doublet of ~118 kHz ($\Delta\nu_{zz}$). This leads to a quadrupolar coupling constant χ of ~161 kHz (eq 2-24), which is characteristic of a D₂CO molecule held rigidly in a lattice. Just

above 145K the line shows a very different lineshape. Between 90-145K, the line shapes correspond to intermediate rates of motion and may be compared with the simulated line shapes of others. The changes in the line shapes occur over the relatively short temperature range of 77K-145K. The fast motion limit (motional rate $\sim 10^8$ jumps/s) is reached at ~ 145 K which suggests that the CD_2 group performs rapid two-fold flips about the molecular C_2 axis between two equivalent sites, and this can be confirmed by the following calculation.

From the general tensor in Euler angles description found elsewhere,¹⁶ in a reference frame with its Z axis along the molecular C_2 axis and averaging over two sites with $\alpha = 0, 180^\circ$ and $\gamma = 0$ (**Figure 3-3**), the relationship between the static and fast motion limit tensor components is

$$a_{11} = \cos^2\beta V_{xx} + \sin^2\beta V_{zz} \quad (3-1)$$

$$a_{22} = V_{yy} \quad (3-2)$$

$$a_{33} = \sin^2\beta V_{xx} + \cos^2\beta V_{zz} \quad (3-3)$$

Since the static tensor is axial ($V_{xx} = V_{yy} = -V_{zz}/2$), these equations can be simplified:

$$a_{11} = (2-3\cos^2\beta) V_{zz} / 2 \quad (3-4)$$

$$a_{22} = -V_{zz} / 2 \quad (3-5)$$

$$a_{33} = (3\cos^2\beta - 1) V_{zz} / 2 \quad (3-6)$$

$$\text{and} \quad (|a_{11}| - |a_{33}|) / |a_{22}| = 3 - 6\cos^2\beta \quad (3-7)$$

where β is the angle between the C-D bond and the C_2 rotation axis; V_{ii} correspond to the principal components of the static tensor, and the a_{ii} corresponds to the average tensor.

Measuring each component from the lineshapes, we obtained;

77K (static)	$\eta = 0$	$V_{xx} = V_{yy} = -120.97 \text{ kHz}$	
		$V_{zz} = +241.94 \text{ kHz}$	
145K (fast motion limit)	$\eta = 0.717$	$V'_{xx} = -19.35 \text{ kHz}$	$V'_{yy} = -117.74 \text{ kHz}$
		$V'_{zz} = +137.10 \text{ kHz}$	

The component of the static tensor perpendicular to the C_2 axis, V_{yy} , should be unchanged by the motion; i.e., a_{22} (V'_{yy}) should take the value of -120.97 kHz , but actually there is a slightly reduction in the YY component according to the fast motion lineshape, this is due to the effects of additional librational averaging.¹⁷ If we keep the same η , but increase V'_{yy} back to its static value, then

$V'_{yy} = -120.97 \text{ kHz},$	$V'_{xx} = -19.94 \text{ kHz},$	$V'_{zz} = +140.91 \text{ kHz}$
----------------------------------	---------------------------------	---------------------------------

Using eq (3-7), the CDC angle can be calculated, i.e., $\beta = 58.15^\circ$, very close to the theoretical value, 58.25° .²³

Figure 3-3 Molecular motion model of formaldehyde

Figure 3-2 Temperature dependence of ^1H NMR lineshapes of D_2CO

(a) Experimental lineshapes; (b) Simulated lineshapes.

The simulations shown in Figure 3-2b are in excellent agreement with the experimental results and permit us to determine a jump rate at each temperature. The simulations were done using the program described in Chapter II. The rate constants obtained from simulated spectra can be used to determine a value for the activation energy for the 2-fold motion of the CD_2 group from a plot of $\ln(\text{jump rate})$ vs $1000/T$ as shown in Figure 3-4, the solid line represents the least-squares fit to the results. The slope of this line yields an activation energy E_a of $23.0 \pm 0.4 \text{ kJ mol}^{-1}$.

Figure 3-4 Arrhenius plot of $\ln(\text{jump rate})$ vs $1000/T$

b. Formaldehyde Hydrate

There is much evidence¹² that the influence of the shape (symmetry) of the individual cages on the guest atoms or molecules gives rise to distinguishing features in the NMR line shapes of the guest in the small and large cages. The small cage of structure I and the large cage of structure II are pseudospherical (have cubic symmetries); the NMR line shapes of guests in these cages are isotropic. On the other hand, the small cage of structure II and the large cage of structure I are oblate ellipsoidal (non-cubic symmetries) and the line shapes of their guests are anisotropic.

Deuterium spectra of D_2CO in H_2O and D_2CO in D_2O were investigated. In the D_2CO / H_2O case, after the deposit was annealed at 150K, the 2H NMR spectrum recorded at 77K turned out to be a single, broad line (width at half height ~ 13 kHz) (Figure 3-5).

Figure 3-5 2H NMR spectrum of D_2CO/H_2O at 77K

Compared to the doublet pattern of solid formaldehyde- d_2 at 77K, the fine structure has disappeared. This disappearance of fine structure implies that the clathrate hydrate is formed and the D_2CO molecule is encaged in the structure I hydrate cages (Figure 3-6), and that leads to a broad, apparently isotropic line shape. The isotropic line broadening can be explained as follows: At low temperatures the water molecules freeze into disordered positions so that a large distribution of slightly different cage configurations is produced. In this regime, the potential experienced by each guest molecule will be different from one cage to the next, the guests thus experience different reorientational motions with the result that the observed guest NMR line shape represents a distribution of individual line shape.¹³

Figure 3-6 Formaldehyde molecules encaged in the sI hydrate lattices

A second sample was prepared with heavy water and formaldehyde-d₂. At 77K, the lineshape (**Figure 3-7a**) consist of a broad component with a doublet ($\chi = 217.8$ kHz, $\eta = 0.096$) corresponding to the static D₂O lattice and a narrower component in the center corresponding to the reorienting D₂CO guest. For D₂O the asymmetry parameter η is close to its value in D₂O ice (**Table 3-2**). Clearly the near identity of the efg tensors of D₂O in ice and clathrate hydrates shows that the hydrogen-bonded OD bond lengths are practically the same.¹⁸ After storage at 77K for 5 months, the D₂O lineshape loses intensity (**Figure 3-7b**). It has been known for some time¹³ that the temperature at which motion of the host water begins is lower when the guest contains oxygen atoms. It is thought that these guests inject Bjerrum defects into the host lattice by the occasional formation of a weak hydrogen bond. The presence of such defects then promotes the water reorientational process by propagating through the lattice. When the sample was annealed at 250K then re-cooled, the ²H NMR lineshape (**Figure 3-7c**) turned out to be a number of overlapping doublets due to decomposition of the hydrate and the hydrolysis of formaldehyde,⁷

The inner doublet ($\chi = 157.6$ kHz) can be assigned to the CD₂ group of the gem-diol of formaldehyde rigidly trapped in a solid matrix while the outer doublet ($\chi = 217.1$ kHz, $\eta = 0.086$) are due to the ice lattice and hydroxyl deuterons.

Figure 3-7 ^2H NMR line shapes of $\text{D}_2\text{O}/\text{D}_2\text{CO}$ (a) at 77K ; (b) after the sample has been stored in liquid nitrogen for five months; (c) sample was annealed at 250k then recooled at 77K

Table3-2 Deuterium quadrupole coupling constants (kHz) and asymmetry parameters

	χ (e^2qQ/h)	η
D ₂ O in ice Ih ¹⁸ , 77K	213.4	0.112
D ₂ O / D ₂ CO, 77K	217.8	0.096
D ₂ O / D ₂ CO (annealing at 250K), 77K	217.1	0.086

c. Effect of Water Reorientation

In general, if some motion with a correlation time, τ , moves the C-D bond of a deuterated molecule isotropically in space and this movement is fast on the NMR time scale (i.e. $\tau < 1 \mu s$), then the 2H spectrum exhibits a Lorentzian shape. The width at half-height, δH , of this single peak is related to the spin-spin relaxation time, T_2 , and contains information characterizing the correlation time of the isotropic motion. The expression for δH is ²⁴

$$\delta H = \frac{1}{\pi T_2} = \frac{3\pi}{4} \left(\frac{e^2 q Q}{h} \right)^2 \left[\frac{3}{2} j(0) + \frac{5}{2} j(\omega_0) + j(2\omega_0) \right] \quad (3-8)$$

where T_2 is the spin-spin relaxation time, ω_0 is the resonance frequency, and $j(\omega)$ are spectral density functions which can be written as:

$$j(\omega) = \sum_i B_i \left(\frac{2\tau_i}{1 + \omega^2 \tau_i^2} \right) \quad (3-9)$$

where τ_i are effective correlation times and the constants B_i are weighting factors which depend on the dynamics of the molecule.

If the molecular motion is an activated process, one has the Arrhenius relation:

$$\tau_i = \tau_0 \exp(-E_a / RT) \quad (3-10)$$

where E_a is the activation energy. Thus the slopes of the $\log(\delta H)$ vs $1/T$ would give the activation energy.

In clathrate hydrate, when the rate of water motion is very slow ($T < 180K$), the water molecules are frozen into static disorder and a distribution of different cages results in a distribution of guest linewidths. When water motion becomes rapid ($>10^4$ Hz), usually at temperatures above $200K^{13}$, the disorder becomes dynamic and can time average all the cages of a particular kind, small or large, become equivalent. The guests then all experience the same potential and thus produce a uniform NMR line shape that is narrower and shows much sharper features than at low temperatures. This quantity can be easily understood from the variable temperature 2H NMR spectra of D_2CO/D_2O (Figure 3-8). At 77K, the lineshape of D_2CO/D_2O consists of a broad component corresponding to the static D_2O lattice with a much narrower (~ 13 kHz) component in the center corresponding to mobile D_2CO guest. As the temperature increases, the D_2O lineshape rapidly loses intensity, with the onset of D_2O reorientation among six possible sites. By $\sim 200K$ the intensity due to the D_2O lattice has collapsed almost completely while the D_2CO guest lineshape remains and sharpens (~ 5 kHz) considerably. For the sample of D_2CO/H_2O , the linewidth also reduces to ~ 5 kHz when $T > 200K$. It has been pointed out¹⁴ that for the structure II hydrate, the average quadrupolar coupling drops to zero at temperatures where the water molecules rotate sufficiently rapidly ($\sim 250K$); the finite residual width is then dipolar in origin. But for the structure I hydrate (as in the

case of formaldehyde hydrate) a corresponding substantial fall occurs but only to an effective coupling constant of several kHz.

Figure 3-8 ^2H NMR spectra of $\text{D}_2\text{CO}/\text{D}_2\text{O}$ as a function of temperature

The activation energy for D_2CO molecular motions in the H_2O or D_2O lattices can be obtained by plotting $\log(\delta H)$ vs $1000/T$ (Figure 3-9). The slope of the least-squares fitting line yield an activation energy of $3.7 \pm 0.1 \text{ kJ mol}^{-1}$ for the motion of D_2CO in D_2O or H_2O lattices.

Figure 3-9 Arrhenius plot of linewidths against temperature for both D_2CO/D_2O and D_2CO/H_2O samples

3.4 Summary

Formaldehyde hydrate was successfully prepared by co-deposition of water vapor and formaldehyde at low temperature and annealed at various temperatures for kinetics studies. X-ray powder diffraction patterns show that formaldehyde forms cubic structure I hydrate with a lattice parameter of 1.1971 nm.

The motions of formaldehyde molecule in the solid state were studied between ~90K and ~150K using pulsed ^2H NMR methods. The static ^2H NMR lineshape of formaldehyde- d_2 below 90K gives rise to a quadrupole coupling constant χ ($= e^2qQ/h$) of 161.3kHz. The lineshape variation with temperature shows that the formaldehyde molecule undergoes fast motion (2-fold flip) even at much lower temperature (reaches fast motion limit at ~150K) with activation energy $23.0 \pm 0.4 \text{ kJ mol}^{-1}$.

The motional behavior of formaldehyde molecules enclathrated in ice frameworks was also studied by ^2H NMR. Both spectra taken for the $\text{D}_2\text{CO}/\text{H}_2\text{O}$ and $\text{D}_2\text{CO}/\text{D}_2\text{O}$ systems show that formaldehyde molecules undergo fast reorientation in the hydrate cages which leads to a singlet ^2H NMR lineshape. Also, the linewidth of the guest molecule resonance narrowed as the temperature increased, thus supporting a dynamic mechanism. From the Arrhenius plot of $\log(\delta H)$ vs $1000/T$, the activation energy of D_2CO reorienting in both D_2O and H_2O can be derived as $0.7 \pm 0.1 \text{ kJ mol}^{-1}$. When hydrate decomposed at about 250K, the distinctive ^2H NMR lineshape indicates that the formaldehyde diol was formed.

Formaldehyde hydrate is the first example of a clathrate hydrate of possible astrophysical significance which, because of the chemistry of the guest, would not be stable under terrestrial conditions. The experiments presented here suggest that formaldehyde clathrate hydrate may act as a storage reservoir for formaldehyde monomer. The exchange between the free molecule and the condensed clathrate hydrate phase is energetically much less demanding than the polymerization-depolymerization cycle which connects the monomer and polymer. There are excellent prospects that it

may be possible to generate other rather unstable guests from precursors by thermolysis or irradiation and that these also may be stabilized inside hydrate lattices at low temperature. Therefore, one may expect to find other unusual and unexpected hydrates in association with icy extraterrestrial environments.

3.5 References

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Chapter IV

Kinetic Inhibition of Clathrate Hydrate

4.1 Introduction

4.1.1 Historic Background of Clathrate Hydrate Inhibition

As described in Chapter I, the formation of gas hydrates can dangerously block pipelines, valves, etc. in gas transmission, gas processing, and deep water drilling systems. Prevention of hydrate formation also is of particular interest to the oil and gas industry which transports unprocessed well-fluid to distant processing locations by pipeline.

Historically, four methods have been used to prevent hydrate formation:⁷

1. Removing water, typically via contacting a hydrocarbon fluid with mono-, di-, and triethylene glycol or molecular sieves,
2. Increasing the system temperature above the hydrate formation point, through heat exchange,
3. Reduction of the system pressure below the hydrate formation point, through pressure depletion or flaring, and
4. Injection of inhibitors such as methanol (MeOH) or monoethylene glycol (MEG) to shift the hydrate equilibrium, so that the system operates in the vapor-liquid region. This method is currently a popular way to prevent hydrate formation.

Hammerschmidt¹ identified gas hydrates as the solids responsible for obstructing gas transmission lines, and conducted early studies on hydrate inhibition using various aqueous solutions of lithium chloride, zinc chloride, calcium chloride, diethylene glycol,

methanol and glycerine. Salts and ionic solutions may, however, cause problems by accelerating corrosion reactions or by precipitation of heavy soluble salts like calcium carbonate. The most common hydrate inhibitors used today in gas transmission pipelines are ethylene glycols and MeOH (at concentrations in the water phase within the range 10 - 60 wt %). These inhibitors act by lowering the activity of water in the aqueous solution, thereby causing a depression (ΔT) of the hydrate forming temperature at a given pressure, and thus thermodynamically inhibit hydrate formation. Typically, the chemical inhibitor is transferred to the wellhead via an injection line from a sub-sea or platform installation. These injection lines are of significant dimensions if large transportation distances and high shut-in wellhead pressures are involved.

However, Makogon² and Berecz and Balla-Achs³ have reported that MeOH in low concentrations (<5 %wt) can, at certain pressure (30-100 bara), act as hydrate stabilizer (raise the hydrate formation temperature). Nakamaya and Hashimoto⁴ reported that MeOH forms gas hydrates of both structures I and II. Davidson et al.⁵ have later reported results of NMR and dielectric studies that contradict the conclusion drawn by Nakamaya and Hashimoto. Nevertheless, as a thermodynamic inhibitor, methanol is considered to be expensive and there are environmental concerns with the disposal of water containing those inhibitors. In addition, in deep sea operations, the ambient operating conditions (low temperature and high pressure) are conducive to hydrate formation. In such cases, the above traditional approaches are be ineffective due to either extreme conditions or high cost.

In recent years an effort has been made to find more effective inhibitors. From the perspective of mechanism of hydrate formation (refer to Chapter I), kinetic methods may be used for hydrate inhibition. Kinetic inhibitors have the following advantages: they can be used in low concentrations, act to prevent the hydrate crystallization and agglomeration, block the hydrate growth, modify the crystals to a transportable size, etc.⁶

4.1.2 Kinetic Inhibitors - Polymers

The use of polymers as inhibitors to influence crystallization and growth has been known for some time.^{14,15} A recent paper dealing with the inhibition of calcium oxalate hydrate formation by some polymers was presented by Manne et al.¹⁶ However, the study of polymers as inhibitors for clathrate hydrate formation is relatively recent.

Unlike thermodynamic inhibitors, kinetic inhibitors only reduce and/or delay the rate of hydrate formation so that hydrate crystals cannot grow beyond small particles and cause plugging on normal oil field or gas transmission line time scales. Such inhibitors potentially could be used at relatively low concentrations (as compared to alcohols), and the inhibitors examined to date are less toxic than conventional hydrate prevention chemicals.⁶

From 1990-1994, several effective kinetic inhibitors have been investigated by the Colorado School of Mines.⁶ These kinetic inhibitors are polymers; no low molecular weight compound has been found to be an effective inhibitor of hydrate growth. **Figure 4-1** shows the structures of some of these kinetic inhibitors. Almost all the kinetic inhibitors found so far contain an amide linkage; the nitrogen substitution pattern appears to be

Primary Inhibitors

Poly(N-Ethyl Arylamide) (PNEAM)

Poly(N,N-Dimethylacrylamide)
(PNNDMAM)

Secondary Inhibitors

Poly(2-Ethyl-2-Oxazoline) (P2E2OX)

Poly(N-Methyl-N-Vinylacetamide) (PNMNVAcAM)

Figure 4-1 Structure of some kinetic inhibitors. (Ref. 6)

influential in inhibitor performance. Some polymers have a ring structure, and those with a caprolactam (7-member) ring are better (called primary) inhibitors than those with a pyrrolidone (5-member) ring are labeled secondary inhibitors.⁶ Some inhibitors do not have a ring structure, but they still have the polymeric backbone and pendant amide group.

The purpose of this work, therefore, was to address several specific questions concerning kinetic inhibitors: (1) how do kinetic inhibitors work? (2) what is the mechanism by which they influence hydrate formation? (3) do they alter the hydrogen bonding of water, and (4) do they adsorb on the surface of hydrate crystals? We present some important preliminary results obtained using NMR and X-ray powder diffraction techniques. Also discussed is the impact of ongoing research and development efforts. Finally, future work is outlined.

4.2 Experimental Section

4.2.1 The Kinetic Inhibitors

The inhibitors used in these experiments were Poly(N-vinylcaprolactam) (PVCap) and Poly(N-vinylpyrrolidone) (PVP); the former is a primary inhibitor and the latter is a secondary inhibitor.⁶ Both samples were supplied by the Colorado School of Mines. Figure 4-2 shows the 300MHz ¹H NMR spectra for (a) PVP and (b) PVCap.

4.2.2 Hydrate System

A simple, straightforward hydrate system was chosen to elucidate the mechanism of kinetic inhibition. Tetrahydrofuran (THF) is the most suitable hydrate-former as it is

Figure 4-2 (a) ^1H NMR spectra of PVP

Figure 4-2 (b) ^1H NMR spectra of PVCap

water-soluble and easily forms hydrate. It forms sII hydrate with a mole ratio of THF: H₂O / 1:17. From the phase diagram of THF-hydrate (Figure 4-3)⁸, the hydrate decomposition temperature along the heavy solid line is 4.4°C above the freezing point of water which distinguishes it from ice.

Figure 4-3 Phase diagram of THF hydrate. (Ref. 8)

Heavy line is the decomposition temperature; Lighter lines are melting points of ices I, III, and V and dashed line separate the regions of stability of different ices

2 OF 2

PM-1 3½"x4" PHOTOGRAPHIC MICROCOPY TARGET
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PRECISIONSM RESOLUTION TARGETS

Since the amounts of kinetic inhibitor used are very small (0.2% - 1% wt), the NMR signal of inhibitor was very weak relative to the THF resonances (**Figure 4-4a**); hence, deuterated THF- d_8 (C/D/N Isotopes, 99.5 atom %D) and D_2O (MSD Isotopes, 99.9 atom %D) were used to make hydrate samples (**Figure 4-4b**).

4.2.3 The Apparatus for Hydrate Formation

The hydrate was prepared using the apparatus shown on **Figure 4-5**. The stirred water bath was controlled by a refrigerated circulation system and a heater (HAAKE, Mess-Technik GmbH u. Co.). The bath temperature was measured with a temperature controller (HAAKE) and was held constant to $\pm 0.05^\circ\text{C}$. The sample tube was lowered into the bath at a constant speed, controlled by a small motor.

4.2.4 Instrumental Techniques

a. ^1H Solution NMR

The making or breaking of hydrogen bonds between water molecules or between water and other components is of great interest for the mechanism of hydrate formation and inhibition. There is a considerable amount of experimental data, (temperature or solvent-dependent measurements on hydrogenous systems) that formation of a hydrogen bond results in downfield shifts of proton resonance from their positions in the unbonded state.^{10,11,12} This kind of hydrogen-bonding interaction may be very useful in the studying of the mechanism of kinetic inhibition of the hydrate.

^1H solution NMR is potentially very useful in studying hydrogen bonding interactions since the chemical shifts are sensitive to the chemical environment.⁹

Figure 4-4 ¹H NMR spectrum of (a) THF/D₂O/PVP; and (b) THF-d₈/D₂O/PVP

Figure 4-5 Apparatus for hydrate formation

In addition, ^1H NMR, due to its high sensitivity, is a relatively rapid method which makes it very suitable for kinetic study. Moreover, ^1H NMR is easy to quantitate. Actually, Davidson et al. first carried out ^1H NMR experiments to study the thermodynamic inhibitor (MeOH); they reported that MeOH is excluded from hydrate,⁵ and thus ^1H NMR spectroscopy may serve as a simple way to classify inhibitors.

Proton NMR spectra were obtained on a Bruker MSL-300 spectrometer using a quadrucycle pulse sequence with a 90° pulse of $6.5\mu\text{s}$ and a delay time of 2s.

b. WIN-FIT Program

Because of the overlapping of the THF and Inhibitor peaks, the WIN-FIT simulation program (Bruker) was used to fit the spectrum in order to get integrated peak intensities for each component. From the intensity ratio of inhibitor to THF peaks, the concentration of inhibitor relative to THF can be quantitatively determined. Figure 4-6 shows both the observed and fitted ^1H NMR spectra for THF- d_8 / D_2O / PVP.

c. X-Ray Powder Diffraction

Since different hydrate structures have different X-ray powder patterns (Chapter I), this method was used to determine whether the kinetic inhibitor modifies the hydrate structure. The X-ray diffractometer used was the same as the one described in chapter III.

4.3 Results and Discussion

4.3.1. Macroexamination of THF-Hydrate With or Without Inhibitor

Sample (a) (b) (c) and (d) were made in small vials with total solution volume of 5.4 ml (Table 4-1).

Figure 4-6 Fitting spectrum for THF-d₈ / PVP / D₂O

One important parameter that affects the time required for initial crystallization is the presence of other particles such as ice or rust¹⁹. The presence of such particles tends to reduce the time required for initial crystallization. Therefore, a piece of ice was first introduced on the bottom of the sample tube, then the sample tubes (a)---(d) were put into cold water (around 3 °C) to condition.

The time for the solution to freeze completely was determined (τ_f). Sample (a) became solid more rapidly than samples (b) and (c); sample (d) was the slowest and was cooled to lower temperatures to shorter the period of conditioning time.

Table 4-1 Macroexamination results

Sample	System	T_{condition} (°C)	$\tau_{formation}$ (hrs)	Physical appearance
a	THF/H ₂ O (mole ratio 1 : 17)	3	3.5	transparent, ice-like
b	THF/H ₂ O + 1 %wt PVP (40K)	3	~ 4.5	white, powder-like
c	THF/H ₂ O + 1 %wt PVP(360K)	3	~ 4.5	white, powder-like
d	THF/H ₂ O + 1 %wt PVCap	3	> 4.5	gel-like

When samples with and without inhibitor are compared, it seems that the sample with inhibitor needs either more time to completely form hydrate, or a lower conditioning temperature. Inhibitor PVCap seems to be a more efficient inhibitor than PVP.

After the solutions become solid completely, the solids' appearances were compared. The appearance differs for the hydrate, probably because of different crystal

size, that is, hydrate without inhibitor forms large crystals (ice-like, transparent), while hydrate with inhibitor forms small crystals (powder-like) (Table 4-1).

4.3.2 Microexamination

a. X-Ray Powder Diffraction

After hydrate formation was complete, samples (a), (b), (c), (d) (Table 4-1) were examined by X-ray powder diffraction at 90°K to further confirm the macroexamination results.

The X-ray diffraction patterns are consistent with sII hydrate for samples (b) and (c) with PVP inhibitor, whereas the diffraction pattern for sample (d) with PVCap inhibitor also shows the presence of ice (Figure 4-7).

X-ray powder diffraction results show that the hydrates with or without inhibitor have the same diffraction patterns, which suggest that the inhibitor does not alter the hydrate structure.

b. ¹H NMR Results

Distribution of Inhibitors:

The distribution of the inhibitor in the different phases (hydrate, ice, solution) can give important clues regarding the mechanism of inhibition and also determines the rate at which inhibitor has to be supplied. Knowledge of the inhibitor distribution in the various phases is therefore essential to develop strategies for hydrate prevention.

Since ¹H NMR is easily quantified, this method is ideal in the study of inhibitor distribution in different phases, that is, to measure the amount of inhibitor associated with

Figure 4-7 X-ray powder diffraction results

the solid hydrate phase relative to the inhibitor remaining in the liquid after hydrate formation

THF-hydrate (THF- d_8 / D_2O 1:17) with different amounts of inhibitor (0.2%, 0.4%, 0.6%, in weight) was grown in a 5 mm NMR tube using the apparatus shown on Figure 4-5. The temperature of the water bath was held constant at 4.5°C. The sample tubes were lowered slowly into the bath at a rate of 1cm/hr.

The initial concentrations of inhibitor in the original solution were determined by 1H NMR before hydrate formation.

In order to separate the solid and liquid phases with minimum exposure to the atmosphere to prevent H-D exchange, we connected two NMR tubes for each sample run. After the hydrates were formed (one-half of the amount of the initial solution) in the solution with inhibitor, we separated the hydrate phase from the remaining liquid solution by pouring liquid phase into the tube on the top and then disconnected the bottom tube (containing solid hydrate). The hydrate phase was then melted and the inhibitor concentration was determined in each phase.

The inhibitor distribution in the solid and liquid phases for (a) PVP(40K), (b) PVP(360K), and (c) PVCAP are shown in Figure 4-8. All three inhibitors show the same distribution behaviour, that is, almost equal concentrations in the solid phase and the liquid phase. It appears that the kinetic inhibitors (PVP, PVCAP) are about equally associated with the solid hydrate phase and the liquid phase, in contrast to thermodynamic inhibitors. Therefore, if the inhibitor is preferentially associated with the liquid phase, it probably is

not a kinetic inhibitor. The effectiveness of kinetic inhibitors appears to depend on a degree of association with the solid phase.

Figure 4-8 Kinetic inhibitor distribution in solid and liquid phase

Studies of Hydrogen-Bonding:

As mentioned before, the water hydrogen chemical shift can be changed by addition of organic solvent, and by changing the temperature.^{10,11,12}

It has been assumed that the properties of water can be treated as a hydrogen-bonded “ice-like” fraction and a non-hydrogen-bonded “monomer” fraction whose interaction with the lattice arises entirely from London dispersion forces.¹² Monomeric water can be the gas phase, or a trace of water dissolved in organic solvent. An enhancement of water hydrogen bonding should yield a downfield shift in the ^1H NMR spectra, since hydrogen bond formation decreases the electronic shielding around the hydrogen nucleus. Therefore, ^1H chemical shifts for monomeric H_2O should be upfield of the pure water shifts, and solid water downfield of the pure water line.¹⁸

The proton chemical shift of water in the THF/water has also been investigated intensively.^{10,11,13} A common result is that $\delta_{\text{H}_2\text{O}}$ shifts upfield upon going from pure water to the infinitely dilute limit in THF. The upfield shift of the water must be explained by the fact that water-water hydrogen bonds are broken and replaced by much weaker hydrogen bonds between water and THF. Clemett¹¹ measured the proton chemical shifts of water over the whole composition range of THF at 34°C (**Figure 4-9**), whereas Glew et al.¹⁰ restricted their experiments to the water-rich region at 0°C and first observed that there was initially a downfield shift of the water proton signal upon addition of THF, with a maximum near 4 mole% THF (**Figure 4-10**), evidence for enhanced solvent water-water H-bonding. It is noted that the two sets of results are not in exact agreement, and there are some concerns about the referencing of chemical shifts.

Figure 4-9 The chemical shift of water proton in THF solution at 34°C (Ref. 11)

Figure 4-10 Water proton chemical shift composition dependence
in aqueous THF (Ref. 10)

So far, no ^1H chemical shift data have been reported for any solid phases of H_2O in a completely hydrogen bonded network.

The information on hydrogen bonding may be taken as evidence of whether or not kinetic inhibitors can affect the hydrogen bonding in solutions of hydrate formers.

(i) ^1H Chemical Shift vs Temperature

An external standard of TMS was sealed in a Pyrex glass capillary for each run. ^1H chemical shifts were measured at various temperatures. The samples used in the experiments and the results are tabulated in **Table 4-2**, data for water (samples a and b) are plotted in **Figure 4-11** and for water/THF- d_8 (sample c and d) plotted in **Figure 4-12** (cooling down) and **Figure 4-13** (warming up).

Table 4-2 $^1\text{H}_2\text{O}$ NMR Chemical Shift vs Temperature

T (K)	D_2O $\delta_{\text{H}_2\text{O}}$	$\text{D}_2\text{O/PVP (0.5\%wt)}$ $\delta_{\text{H}_2\text{O}}$	$\text{D}_2\text{O/THF-}d_8 \text{ (17:1)}$ $\delta_{\text{H}_2\text{O}}$		$\text{D}_2\text{O/THF-}d_8\text{/PVP}$ $\delta_{\text{H}_2\text{O}}$	
293	4.6343	4.6050	4.6245		4.6148	
289	4.6898	4.7340	4.6656		4.6930	
285	4.7634	4.7614	4.7497		4.7497	
281	4.8318	4.8318	4.8318		4.8220	
277	4.9061	4.9159	4.8944		4.8885	
273	4.9824	4.9843	4.9687		4.9491	
269	5.0430	4.9374	5.0098		5.0293	
265	4.9198	4.9374	6.2905	4.8377	6.3316	4.8145
warm up						
269					6.2710	
273			6.2749		6.2614	
277			6.2358	4.7340	6.2084	4.7301
281			6.1693	4.8553	6.1674	4.8416
285			6.1595	4.8435	6.1439	4.8396
289				4.6910		4.6441
293				4.6226		4.6206

The Figure 4-11 shows that ^1H chemical shift for D_2O and $\text{D}_2\text{O}/\text{PVP}$ at various temperatures have the same trend: as the temperature decreases, the chemical shift moves downfield, which suggests the water-water hydrogen bonding interactions become stronger, PVP did not change this interaction significantly.

Figure 4-11 $^1\text{H}(\text{water})$ chemical shift vs temperature for D_2O and $\text{D}_2\text{O}/\text{PVP}$

**Figure 4-12 ^1H (water) chemical shift vs temperature (cooling down)
for $\text{D}_2\text{O}/\text{THF-d}_8$ and $\text{D}_2\text{O}/\text{THF-d}_8/\text{PVP}$**

Figure 4-13 ^1H (water) chemical shift vs temperature (warming up)

for $\text{D}_2\text{O}/\text{THF-d}_8$ and $\text{D}_2\text{O}/\text{THF-d}_8/\text{PVP}$

For the sample with THF-d₈ (c, d), a phase transition occurs at 265K from the supercooled liquid to the solid hydrate when temperature is decreased (Figure 4-12). On warming the sample, two phases, the aqueous liquid, and the THF-hydrate solid phase, co-existed in the temperature range 277K - 285K (Figure 4-13). This is the first observation of ¹H chemical shift for the solid phase in THF hydrate system. The shift of ~6.3ppm is much larger than any shift measured for water in the liquid, even in the highly supercooled state.²⁰ When the previous results for the monomer water chemical shift is compared (which remained almost unchanged with variation of temperature as shown by the line on the bottom in Figure 4-13), one may conclude that the H-bonding of water which forms the hydrate cavities is indeed stronger. Addition of PVP does not change the ¹H chemical shift behaviour in the THF-d₈ solution.

(ii) ¹H Chemical Shift Studies in D₂O / THF-d₈ Mixture with Inhibitors

For further confirmation, ¹H chemical shifts were measured for the mixture of D₂O/THF-d₈ with various concentration of sea salt, PVP and PVCap at room temperature (Table 4-3, Figure 4-14).

Table 4-3 Chemical shift of water in THF-d₈/D₂O with salt, PVP, PVCap

Salt(%wt)	¹ H δ _{ppm}	PVP (%wt)	¹ H δ _{ppm}	PVCAP (%wt)	¹ H δ _{ppm}
0	4.6148	0.1	4.6109	0.1	4.6069
1	4.5854	0.2	4.6011	0.2	4.6128
2	4.5659	0.4	4.6011	0.4	4.6118
3	4.5445	0.6	4.6001	0.6	4.6069

Figure 4-14 ^1H chemical shift (water) vs concentration of inhibitors

From the plots in Figure 4-14, the ^1H chemical shift in the THF solution with salt (electrolyte) changed with the increase of the salt concentration. The upfield shift may be due to salt placed in the solution whose dissolved ions decreased water-water hydrogen bonding interactions.¹⁷

For the THF solution with PVP and PVCAP, the ^1H chemical shift of water remains unchanged which further confirms that the PVP and PVCap do not affect H-bonding of water solution at the concentrations used.

4.4 Summary and Future Work

Kinetic inhibitors (PVP and PVCap) have been primarily studied by ^1H NMR and X-ray powder diffraction techniques to understand the mechanism of kinetic inhibition on hydrate.

Macroexamination results show that the sample with the kinetic inhibitor takes more time or a lower conditioning temperature to form hydrate than the sample without inhibitor. The hydrate appearance also differs for samples with or without inhibitor, that is, a sample without inhibitor seems to form larger hydrate crystals than a sample with inhibitor.

X-ray powder diffraction results give the same hydrate pattern for all samples tested showing that the kinetic inhibitors do not change hydrate structure type. The kinetic inhibitor distribution behavior has been studied by ^1H solution NMR. It appears that kinetic inhibitors (in the case of PVP and PVCap) at the concentrations studied are about equally associated with the solid hydrate phase and the liquid phase. Finally, the hydrogen-

bonding interaction of water in THF solution was investigated at various temperature and/or varied inhibitor concentration. The same trend of chemical shift for both sample with and without inhibitor has been seen.

From the experimental results we could primarily conclude that kinetic inhibitors (PVP and PVCap) may not stop the hydrate formation but slow down the rate of nucleation and control the growth of hydrate, hence do not change the hydrate structure. Since kinetic inhibitors do not alter the hydrogen bonding capacity of water, it may adsorb on the growth planes of the initial hydrate particles. In such case, crystal particle growth rates on these surfaces are then inhibited and crystal growth is forced to occur on the slower growth planes and thus slowing the formation rate of hydrate.

The benefits of the kinetic inhibitors (such as PVP and PVCap) are that significantly less chemical is required (100x reduction) for inhibition and they are less toxic than conventional hydrate prevention chemicals. Hence, minimum precautions are required for handling it. The addition of the PVP polymer to the gas production and transportation facilities did not cause any operational problems in the cases studied.⁶ Therefore, gas hydrate problems might be controlled by polymeric additives (kinetic inhibitors), although the "ideal" inhibitor remains unknown. One may expect that, in the near future, kinetic inhibitors might replace methanol as hydrate inhibitors in the gas industry.

This is the first time that ^1H NMR has been used to study the mechanism of kinetic inhibition. The results presented are consistent with a surface blocking mechanism, however, it is clear that additional work is needed.

A scheme for hydrate formation that can be proposed is:

Nucleation: solution precursor (cluster) <----> crystal nucleus ----> hydrate crystal

Growth: hydrate crystal + solution ----> larger crystal

hydrate crystal + hydrate crystal ----> larger crystal

Inhibition: hydrate crystals + inhibitor <----> hydrate with surface adsorbed inhibitor

----> larger crystal

Within the above scheme there remain a large number of unknowns, eg. the nature of the cluster precursor in solution, and the nature of the crystal with surface adsorbed inhibitor. The latter is perhaps most amenable to study, by identifying the crystal faces which grow under specific conditions. Another possibility is the study of solution structure in order to identify precursors either by looking at dynamic properties (NMR relaxation), or by measuring radial distribution functions.

4.5 References

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