

**INVESTIGATIONS INTO THE STABILITY, MORPHOLOGY
AND THE CRYSTAL STRUCTURE OF STRUCTURE I AND
STRUCTURE II METHANE-ETHANE CLATHRATE HYDRATES**

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ABSTRACT

Gas hydrates (clathrates) are elevated-pressure (P) and low-temperature (T) solid phases in which gas molecule guests are physically incorporated into hydrogen-bonded, cage-like ice host frameworks. High pressure, low temperature clathrate experiments are carried out on the High Pressure Preferred Orientation (HIPPO) beam line at the Los Alamos Neutron Scattering Center (LANSCE) on methane-ethane hydrates. Neutrons are particularly sensitive to hydrogen and deuterium and they present a significant advantage for investigating the aqueous chemistry of dissolved gases because hydrogen atoms represent 2/3 of the atoms in aqueous solutions.

Methane and ethane are each known to form structure I hydrate, but when mixed, can form sII hydrate under certain conditions. I will synthesize a wide range of compositions and perform gas chromatography to determine gas composition, and look at crystal morphology and growth mechanisms of these clathrates using a cryostage Scanning Electron Microscope (SEM). A combination of neutron and X-ray diffraction will be performed over the full range of relevant P and T conditions to determine the stability field of each of the compositions.

Keywords: gas hydrates, neutron diffraction, methane-ethane hydrate, Los Alamos

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INTRODUCTION

Gas hydrates (clathrates) are elevated-pressure (P) and low-temperature (T) solid phases in which gas molecule guests are physically incorporated into hydrogen-bonded, cage-like ice host frameworks. Natural clathrates have been found worldwide in permafrost and in ocean floor sediments, as well as in the outer solar system (the Moon, comets, Mars, satellites of the gas giant planets). Clathrates in oceanic deposits have a great potential as an energy resource for the future; some have estimated that the global reserve of methane in hydrate form contains more than twice the energy of all natural gas, petroleum, and coal deposits combined [1]. However, clathrates in these deposits exist in rather delicate equilibrium conditions, and certain perturbations, such as depressurization and/or warming can cause decomposition into methane gas and water. This reaction has significant implications for clathrate exploitation since methane released to the atmosphere due to destabilization of ocean-floor hydrates could exacerbate greenhouse effects and potentially contribute to global warming.

Crystal Structure

Three distinct clathrate structures have been identified, sI, a primitive cubic structure that forms with smaller gas molecules at moderate pressures; sII, a diamond-like structure in a face-centered cubic framework that forms with molecules larger than ethane but smaller than pentane; and sH, a hexagonal framework structure that incorporates larger molecules (up to 8Å) such as components of gasoline [2]. A fourth structure has been described recently, the sIII structure [3], which can be described as an orthorhombic filled ice structure.

SAMPLE PREPARATION

All samples used for this study was synthesized at the United States Geological Survey, in Menlo Park, California using the method developed by Kirby, Stern et al. [4,5]. This method has proven valuable for

successful growth of polycrystalline hydrate specimens with controlled and uniform grain size. A similar synthesis setup is being constructed at LANSCE for future clathrate synthesis work.

NEUTRON DIFFRACTION

Introduction

Neutrons are particularly sensitive to hydrogen and deuterium and they present a significant advantage for investigating the aqueous chemistry of dissolved gases because hydrogen atoms represent 2/3 of the atoms in aqueous solutions and because clathrate structures are determined by hydrogen-bonding. Neutron diffraction yields precise structural information on atomic positions, inter-atomic distances, and atomic thermal vibrations under a variety of experimental conditions, providing information on the nature of bonding and thermal vibration of hydrogen atoms. Neutrons' penetrating power and the lack of angular drop-off in scattering cross sections make them superior to X-rays in these structural studies.

HIPPO- High Pressure Preferred Orientation

High pressure, low temperature clathrate experiments are carried out on the High Pressure Preferred Orientation (HIPPO) beam line at the Los Alamos Neutron Scattering Center (LANSCE). The High-Pressure Preferred Orientation neutron time-of-flight diffractometer, HIPPO for short, was designed and constructed at the Los Alamos Neutron Science Center (LANSCE) in 1998. Key specifications of HIPPO are its 8m incident flight-path, viewing a low-resolution, high-flux neutron moderator of the pulsed spallation neutron source at LANSCE. After passing an adjustable collimator, allowing beam-spot sizes of 5, 10, 15, 17, and 20 mm in diameter, neutrons interact with the sample. Figure 1 shows

the detector system consists of 1360 ^3He detector tubes arranged in panels on rings of 150° , 90° , 40° , 20° , and 10° diffraction angles around the incident beam direction.

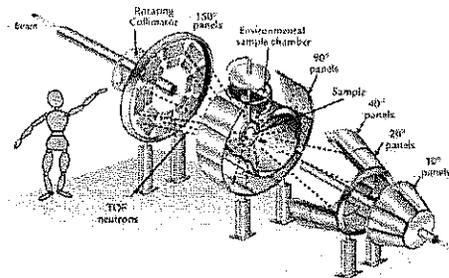


Figure 1. Schematic of HIPPO showing the different sets of detector banks at the Los Alamos Neutron Scattering Center.

Ancillary equipment on HIPPO

Neutron clathrate hydrate research at LANSCE can be performed in a variety of apparatuses, namely the ZAP cell, an Al-gas cell, a top-hat Al-high pressure cell, and a low temperature dispex.

The ZAP cell is a large volume moissanite (SiC) anvil cell. The moissanite anvils are weakly absorbing and provide higher neutron flux to the sample than is possible with tungsten carbide anvils. The ZAP cell can be used for ultrasonic, Raman or diffraction work.

An Al-gas cell that was originally fabricated at Argonne National Laboratory was later duplicated at Los Alamos National Laboratory [6]. The cell is made of an aluminum alloy and is intended for use with pressures up to 70 MPa at room temperature or below which is used mainly for kinetic-type studies.

The top-hat Al-high pressure gas cell is attached to the closed-cycle cryostat and

surrounded by two temperature shields, allowing its cooling down to 4 K. The cell pressurizes indirectly via thin high-pressure tubing coming through a standard vacuum connector.

METHANE-ETHANE HYDRATES

Natural gas hydrates form in oceanic sediments and permafrost from a gas mixture that contains primarily methane (CH_4) as well as ethane (C_2H_6), propane (C_3H_8), and other gases in smaller amounts. Several studies to-date have been done on "pure" systems of gas clathrates (ex. methane [7], CO_2 [8] and propane[9]) but very few studies have focused on mixed gas systems that form clathrate hydrates in Nature.

Subramanian et al. [10] and others report that methane and ethane are each known to form structure I hydrate (figure 2), but when mixed, can form sII hydrate under certain conditions (figure 3). For this study we will synthesize several methane-ethane clathrates over the whole range of compositions (100% end member, 90-10%, 80-20% etc.). After synthesis we use gas chromatography to determine the final gas composition of the clathrates (which might vary in the synthesis procedure) and look at crystal morphology and growth mechanisms of these clathrates using a cryostage Scanning Electron Microscope (SEM). A combination of neutron and X-ray diffraction will be performed over the full range of relevant P and T conditions to determine the stability field of each of the compositions.

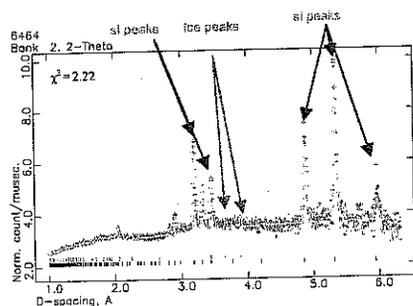


Figure 2. Neutron diffraction pattern of ethane hydrate (D_2O) on HIPPO.

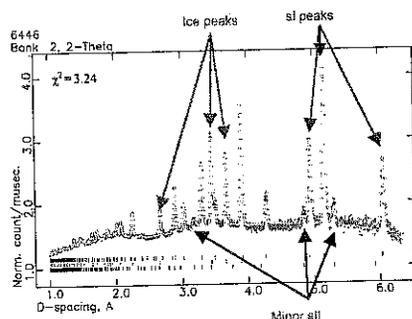


Figure 3. Neutron powder diffraction pattern of methane-ethane (90/10) (D_2O) on HIPPO.

CONCLUSIONS:

Ultimately, studying changes in the crystal-structure of clathrate hydrates under varying pressure and temperature ranges a) will help explain the environmental consequences of global warming on natural gas hydrates; b) will further the understanding the formation of large bodies in the outer solar system, such as Titan, Saturn's largest moon, and c) lead to better techniques of extracting natural clathrates from the ocean floor to increase the global energy supply.

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