NEUTRON DIFFRACTION MEASUREMENTS OF THE NUCLEATION AND GROWTH MECHANISMS OF METHANE HYDRATE.

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Abstract.

In this paper we present the results of our *in-situ* x-ray and neutron diffraction experiments during the formation of gas hydrates under industry operating conditions. We have performed energy dispersive x-ray diffraction to investigate the crystalline nature of species formed during the hydrate formation process. These experiments have been performed on carbon dioxide and propane hydrate. We show that Bragg peaks, indicating crystal structures, appear during the formation process. Some of these peaks appear in the final hydrate diffraction pattern and others do not. However, in the intermediate stages there is a lot of amorphous structure which could not be interpreted. In an effort to understand this part of the formation process we have performed neutron diffraction experiments on the Small Angle Neutron Diffraction for Amorphous and Liquid Samples (SANDALS) instrument at the Rutherford Appleton Laboratory. This instrument is designed to look at short range structure and provides information on the water structure around the guest molecules in the liquid phase. We present examples of the solvation sphere around methane molecules during the formation of methane hydrate, together with the average size and variance of the co-ordination sphere

Introduction.

A substantial body of information is now available on the equilibrium properties of clathrate hydrates [1-5]. This data has been collected over several decades during which it has been used to support the development of fundamental models to explain chemical and engineering aspects of gas hydrate knowledge [6]. However, these properties and the information currently available fail to identify the mechanisms through which gas hydrates nucleate, grow or decompose, and in some cases fail to accurately determine the thermodynamic properties. Hydrate research has recently concentrated on the kinetics of gas hydrate formation. The methods for the prevention of hydrate formation have also concentrated on kinetic control rather than thermodynamic control.

The work described in this paper uses x-ray and neutron diffraction to investigate the structure in liquid water before and during hydrate formation. We have used the Energy Dispersive X-Ray Diffraction (EDXD) instrument at the Daresbury Laboratory to monitor the formation and decomposition of gas hydrates. We have also used the SANDALS (Small Angle Neutron Diffraction of Amorphous and Liquid Samples) at the Rutherford-Appleton Laboratory to monitor structure in the liquid phase before and during hydrate growth.

Methodology.

Both types of experiment have been conducted in specially designed high pressure cells. Temperature, pressure and composition were selected and controlled throughout the experiments. The experiments were conducted *in-situ*, such that gas consumed during hydrate formation is replaced by gas from the cylinder and the pressure maintained.

The x-ray diffraction experiments were carried out over a 250 to 300 K temperature range and 0.1 to 3.5 MPa pressure range [7,8]. The detector angle was fixed at 5.042°. *In-situ* experiments were conducted for carbon dioxide/water and propane/water systems. Diffraction patterns were recorded every 200 second throughout the experiments. Data was collected as a series of intensity *vs.* energy spectra recorded with time throughout the experiments.

The neutron diffraction experiments on the methane/water system were carried out at constant pressure (2100 psi) and the temperature varied using a ramping procedure. Two scattering patterns were recorded at each temperature. The first stage of the experiment was carried out at a temperature in the water/gas region of the phase diagram (291 K). The scattering pattern was recorded over a 30 minute period. The temperature was reduced to a point within the hydrate region of the phase diagram (283 K). Further scattering patterns were obtained. The temperature was further reduced to 277 K and subsequently reduced to 263 K were the complete sample was frozen. Any ice obtained was melted by reheating to 277 K, where the final scattering patterns were obtained.

Spherical Harmonic Analyses were performed to obtain detailed views of the local intermolecular orientational correlation function [9-11]. Reverse Monte Carlo (RMC)

simulations were performed on one scattering pattern at each of the four temperature set points (291 K, 283 K, 277 K (cooling) and 277 K (heating)). The original simulation cell contained 12 methane molecules and 1500 water molecules arranged in a random configuration. The RMC simulation were carried out over 5 million trials, using an empirical water model. The results for the RMC simulations were deemed to be more realistic than our previous results using a Spherical Harmonic Reconstruction [9-11].

Results.

The EDXD experiments lead to some interesting preliminary results. In figure 1, we show the diffraction patterns taken during an experiment. At time zero, the diffraction pattern indicates an amorphous sample, *i.e.* the liquid and gas mixture. As the experiment progresses, sharp peaks appear in the diffraction pattern. These peaks are due to Bragg reflections from a crystalline material. The final pattern is comparable with the diffraction pattern of the complete hydrate structure. That is, the calculated unit cell length is in agreement with literature values and the indexed peaks correspond to Bragg reflections obtained from the single crystal diffraction patterns.

The intermediate stages of this experiment are more difficult to interpret (see figure 2). These diffraction patterns contain a mixture of amorphous and crystalline species. At present, we cannot determine whether Bragg peaks in these intermediate stages which do not appear in the the final hydrate are due to a preferred orientation effect or a crystalline intermediate, which may or may not exist in some form in the product. Methods for interpreting these intermediate stages are currently under investigation.

The EDXD experiments are primarily designed to look at definite crystal structures, as the x-rays are diffracted by planes of electron density in the crystal. Neutrons, on the otherhand, are diffracted by atomic nuclei and therefore provides the possibility of investigating short-range order in liquids. The data shown here were subjected to a spherical harmonic analysis to assess the degree of orientational correlation of water around the methane. The first term in this series expansion of the data is simply the centres correlation function, methane carbon to water oxygen. This is shown in Figure 3 for the four cases. A pronounced co-ordination sphere is found in all instances, but changes quite abruptly for case (4) when a significant amount of methane hydrate is formed. It can be seen from cases (1) - (3), the co-ordination sphere peaks at an average distance of about 3.6 A for case (1) and then gradually moves to larger radius values as the water/methane system is pushed towards the formation of hydrate by decreasing of temperature. The fits that were obtained are shown in figures 4 and 5.

The RMC simulations aim to reproduce the total corrected scattering pattern of the sample. In figure 3, we show the CH_4-O pair correlation function obtained from the scattering patterns obtained at each of the four temperatures described above. The changing correlation function from (a) to (d) indicates an increase in the average number of water molecules in the co-ordination sphere around methane. This is taken from the area under the first peak in the pair correlation function in each case. The position of the peak also indicates that the co-ordination sphere contracts in radius as the experiment progresses. These distances have been used to extract examples of the co-ordination spheres from the final RMC structures. The regions extracted from these structures give some indication of the water structure around the methane molecules during each stage of the experiment. Firstly, we should point out that the number of water molecules within the required distance of the methane molecules is not the same for each methane at each stage of the experiment. The area under the first peak in the pair correlation function indicates the average number of water molecules in the first co-ordination sphere. In Table 1 we present the average and variance of the number of water molecules in the co-ordination spheres for each stage of the experiment. It is interesting to note that there are distorted ring tetramers, pentamers and hexamers in these structures. It is noticeable that the average number of water molecules in the co-ordination spheres increases from part (a) to part (d). This is a consequence of hydrate formation where the expected average number of water molecules in the co-ordination sphere is 23 assuming full conversion to hydrate.

Conclusions

We have demonstrated that the use of energy dispersive x-ray and small angle neutron diffraction techniques can provide complementary information on the formation of natural gas clathrate hydrates.

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Figure 1:
x-ray diffractogram for carbon dioxide hydrate.

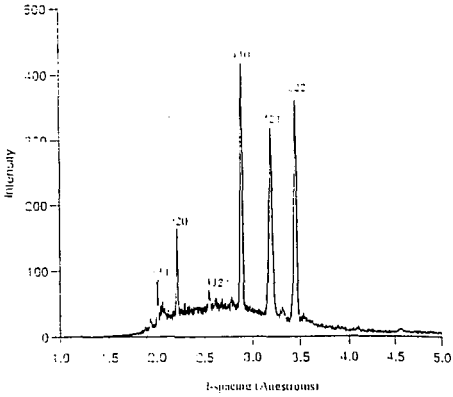


Figure 2:
x-ray diffractograms for carbon dioxide hydrate growth.

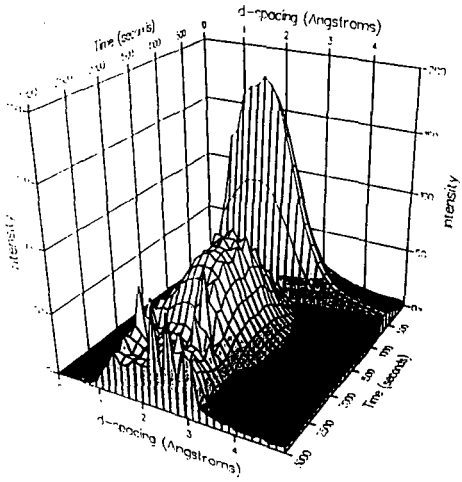
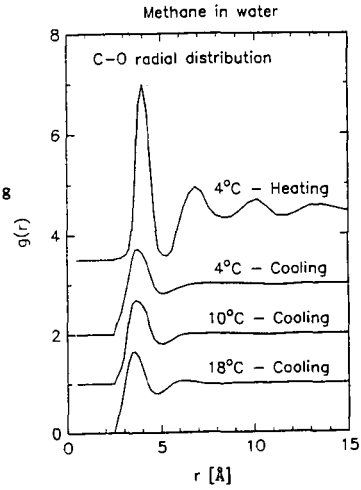


Figure 3:
radial distribution functions for methane carbon and water oxygen during methane hydrate growth.



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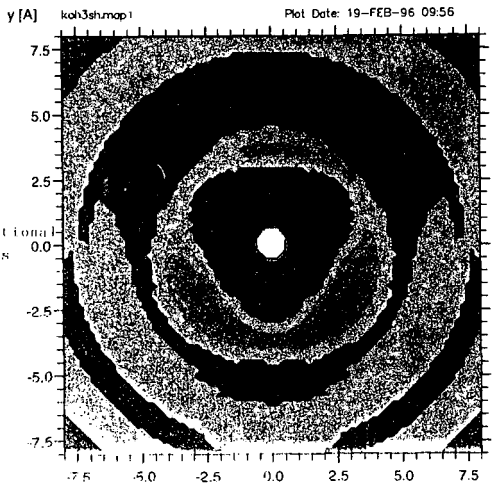
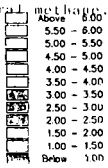


Figure 4 orientational diagram for H atoms of water around a central methane.



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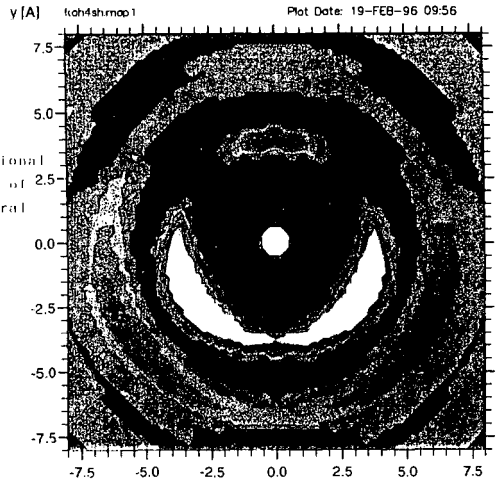
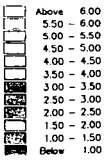
Figure 5 orientational diagram for H atoms of water around a central methane.