

CLATHRATE HYDRATES: SOME NEW STRUCTURAL INFORMATION*

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INTRODUCTION

The accurate prediction of conditions for hydrate formation depends strongly on the availability of good structural information¹. For clathrate hydrates, a complete description of structure involves not only the unit cell parameters and average atomic positions, but also the cage occupancies. In order to provide this kind of information, it is necessary to use techniques such as diffraction, which is sensitive to long range order, in combination with techniques such as NMR which are sensitive to local order². Previously we have demonstrated the use of NMR methods for the determination of relative cage occupancies for structure I and II hydrates³.

Although the crystal structures of Str. I and II hydrates have been known for a considerable length of time⁴, the detailed lattice information on Str. H hydrate has remained unknown until recently⁵. It is also remarkable that a number of other apparently simple clathrate hydrate structures remain unsolved. Examples are the low hydrate of dimethyl ether⁶ and bromine hydrate. The latter is especially intriguing as the hydrate was first reported in 1829⁷, and it has been studied on and off for over 160 years⁸. A crystal space group and a set of lattice parameters were reported by Allen and Jeffrey⁹, although atomic coordinates were not obtained. More recently, Dyadin and co-workers⁸ have claimed that on the basis of hydration numbers which range from ~ 7 to 12, and the different crystal morphologies reported that there is evidence for as many as four different structures. We have now shown that a single crystal structure accounts for all of the different hydration numbers and crystal morphologies.

Another factor that is relatively unappreciated is the fact that although the small 5¹² (D) cage is common to all 3 structures, I, II and H, the symmetry and size of these small cages is different¹⁰, and hence their behaviour towards guest molecules should also be quite different. This is very directly evident from the chemical shift parameters of xenon trapped in the small cages which suggest that the structure II and H small cages are significantly larger and less symmetric than the Structure I small cage. Experiments with CO₂ have confirmed this idea.

Experimental

Bromine hydrate single crystals suitable for diffraction were grown from solutions of different concentrations to give material of different morphologies and hydration numbers see table 1. The crystal structures were determined on a Siemens diffractometer equipped with a CCD detector using Mo K_α radiation. In all, 16 different crystals were examined. The structures were solved with the Shextl software package.

Double hydrates of xenon or ¹³CO₂ were made by sealing into 10mm pyrex tubes measured quantities of powdered ice, along with the appropriate large cage and small cage guests. Samples were conditioned for times lasting from ~ 1 day to several weeks. NMR spectra were measured on an Bruker MSL 200 spectrometer equipped with a double-tuned solenoid probe suitable for cross-polarization and dipolar decoupling². Temperature variation was achieved with a cold gas-flow system and a temperature controller. Spectral simulations were carried out with the Bruker Xedplot package.

RESULTS AND DISCUSSION

a) The structure of bromine hydrate

As was pointed out in the introduction, bromine hydrate can be made with different hydration numbers and vastly different morphologies⁸. Hydration numbers have been reported by at least 13 different authors and vary from 7 to 12⁸. For the crystals used in this study, the composition of the crystals was controlled by changing the concentration of the starting solutions from (Br:H₂O) 1:20 to 1:5. (table 1). The morphology of the different crystals is shown in fig. 1. Six crystals were studied in detail in order to come to a satisfactory solution of the structure, the space group and cell parameters for ten

other crystals were determined to cover the different crystal morphologies. For all of the crystals studied, the space group turned out to be the one reported by Allen and Jeffrey⁹: $P4_2/mnm$. At -100°C the lattice parameters are $a=23.044$, $c=12.075$ Å.

One view of the structure is shown in fig.2. The unit cell can be represented¹¹ as follows: $2D_A, 8D_B, 8T_A, 8T_B, 4P, 172H_2O$ with a $5^{12}6^3$ (P) cage, two distinct $5^{12}6^6$ (T_A , T_B) cages similar to those in str. I, and two kinds of 5^{12} (D_A , D_B) cages. The reason for the difficulty in finding a good structural solution becomes apparent when examining the guest positions in fig. 2. As opposed to structures with hydrocarbon guests, in the bromine hydrate case the scattering is dominated by the highly disordered bromine guest: the P cage has as many as 12 possible positions for bromine; the T cages each have 14 (T_A) or 15 (T_B), with the site occupancies varying from 20 down to 2 %. The highly anisotropic site distribution is evident especially for the T cages, where the centre of the cavity can be seen to be clear as the bromine atoms are confined to be near to the equatorial plane of the cage. The variable hydration numbers observed for bromine hydrate arise from the variable degree of filling of the large cages (table 1). The minimum hydration number possible is 8.6.

It will be another challenge to work out a thermodynamic model for bromine hydrate, as the clathrate has 3 types of large cage (P, T_A , T_B) suitable for bromine, and two small cages (D_A , D_B) which may contain oxygen or nitrogen from the air (some electron density in the small cages was indeed observed). The bromine hydrate structure is the only one of its type, as all other molecules of this size form str. II hydrate. Attempts to form a different hydrate with xenon as helpgas initially gave a structure II hydrate, but with time this was seen to revert back to the bromine hydrate structure. The fact that the large cages do not need to be full seems to be unique as well. This suggests that guest - guest interactions may play an important role in dictating structure type. Significant guest - guest interactions are likely for the electron-rich bromine molecule which should have a sizable molecular quadrupole moment. Another challenge is the understanding of the reasons for the different crystal morphologies. It appears that some kind of "self-inhibition " takes place to suppress the growth of certain crystal faces when the bromine concentration varies in the growth solution.

b) NMR Chemical Shifts and Cage Size

One of the first applications of ^{129}Xe NMR spectroscopy was the chemical shift resolution of the distinct sites in str. I hydrate². It was also noted that the chemical shifts for the 5^{12} cages in str. I and II were quite different¹⁰. According to the empirical chemical shift - cage size relationship, the D cage in str. II is larger than that in str. I. Since little is known about potential helpgases for str. H, it was thought that the Xe NMR parameters could give some guidance for the prediction of the suitability of CO_2 as such a helpgas for the two small cages. ^{129}Xe chemical shift for different hydrate cages are summarized in table 2 along with the point symmetry of the cages.

We note that str. I has the only pseudospherical D cage. From the chemical shift data, the other D cages are not only less symmetric, as indicated by non-zero chemical shift anisotropies, but also somewhat larger, as seen from the smaller shifts. This is likely to be of some importance for all small cage guests, since in str. I the fact that the small cage occupancy decreases with increasing guest size suggests that it is the repulsive interactions that limit the cage occupancy. Also, especially for non-spherical guests small departures from spherical symmetry are likely to be important. CO_2 is a good test molecule, as it appears to be a marginal guest for the 5^{12} cages. An indirectly determined hydration number from thermodynamic measurements is 7.0^{12} , which leads to an occupancy ratio $\theta_g/\theta_c \sim 0.3$ through the relationship between hydration number and guest occupancy ratio once the free energy difference between the hypothetical empty lattice and ice is known³. In a previous NMR study¹³, small cage CO_2 guests were not observed, as the central region of the spectrum is dominated by contributions from liquid and/or gaseous CO_2 . By using the appropriate polarization transfer pulse technique, these contributions can be eliminated from the spectrum, leaving the small cage contribution visible (fig. 3 (top)). On the other hand, for a double hydrate of propane and CO_2 , the ^{13}C spectrum indicates that nearly all of the CO_2 molecules are now located in the 5^{12} cage, that, from the Xe spectrum, is slightly larger and shaped like an oblate spheroid. The very weak central line indicates that there is almost no CO_2 in the large cage of the hydrate. The two propane ^{13}C resonance lines aren't resolved and occur as a single peak at ~ 18 ppm.

Based on these observations, what would one expect for the Str. H small cages ? From the ^{129}Xe spectra, the D and D' cages should be as large as the str. II D cage and

also quite asymmetric. An attempt was made to produce a hydrate sample of neohexane with CO₂ as small cage guest. The product gave the ¹³C spectrum shown in fig. 4. Indeed, contributions can be found from CO₂ in both D and D' cages with NMR lineshapes characteristic of axial and non-axial symmetry. We can conclude that CO₂ is indeed suitable as a small cage guest in str. H hydrate.

CONCLUSIONS

The long outstanding problem of the structure(s) of bromine hydrate has been solved successfully by examining 16 crystals of different morphologies and hydration numbers. There is just one structure, now solved in detail, and it is the tetragonal form originally suggested by Jeffrey.

By using the Xe NMR spectrum observed for xenon trapped in the small cages in str. I, II and H, it was predicted that the small cages in str. II and H should be good sites for CO₂. This was confirmed by using ¹³C NMR spectroscopy to examine a number of CO₂-containing hydrates. CO₂ is now also confirmed as a possible helppgas molecule for the structure H hydrate. The fact that all of the small cages (D and D' in str I, II and H) have different shapes and sizes (especially as defined by ¹²⁹Xe NMR) suggests that the Langmuir constants which define the affinity of small guests for these cages should also be different.

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Table 1. Some details on the crystals of bromine hydrate studied

Initial composition of solution (Br ₂ :H ₂ O)	Average degree of filling of large cavities* (P, T _A , T _B)	Crystal Stoichiometry* (Br ₂ :H ₂ O)
1:20	0.805	1:10.68
1:14	0.914	1:9.41
1:10	0.946	1:9.09
1:7	0.962	1:8.94
1:5	0.998	1:8.62

* from analysis of crystal structure data

Table 2. Hydrate cages, cage sizes and ¹³⁵Xe chemical shift data

Structure	cage type	symmetry	radius/Å ^a	σ _{iso} (iso) ^b (ppm)	δ° (ppm)	η ^d
I	5 ¹² (D)	m3	2.50	-242	0	
I	5 ¹² 6 ¹ (T)	42m	2.93	-152	-21	
II	5 ¹² (D)	3m	2.50	-231	-16	
II	5 ¹² 6 ⁴ (H)	43m	3.28	-80	0	
H	5 ¹² (D)	mmm	2.50	-231	-13.6	0.8
H	4 ⁵ 5 ⁶ 6 ¹ (D')	62m	2.50	-212.4	-31.8	
H	5 ¹² 6 ³ (E)	6/mm	4.1	-----	-----	

^a estimate from X-ray diffraction data; ^b isotropic chemical shift; ^c δ=(2/3)Δσ - chemical shift anisotropy; ^d asymmetry parameter - departure of cage geometry from axial symmetry

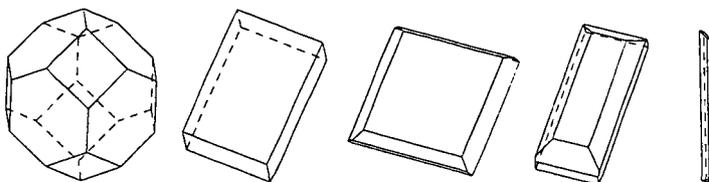


Figure 1. Morphology of different bromine hydrate crystals studied. In general, the massive form is seen most readily in dilute solutions, the needles in concentrated solutions.

Figure 2. General view of the bromine hydrate structure with the view approximately along the z direction; hydrogen atoms are omitted for clarity; the bromine atoms are shown in their many possible disordered positions in the cages, the maximum occupancy being one molecule per cage

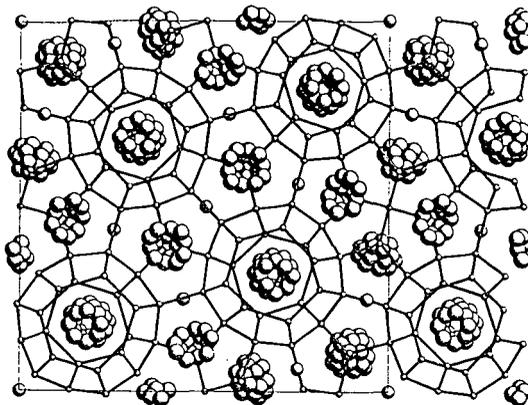


Figure 3. ^{13}C NMR powder patterns obtained for a) CO_2 hydrate b) double hydrate of CO_2 and propane. Note that the symmetry rather than the cage size determine the chemical shift patterns which reflect the nature of the guest motion (isotropic vs anisotropic). Pseudo-spherical cages give the sharp central lines (since cross-polarization methods were used, the liquid and gaseous CO_2 are not visible).

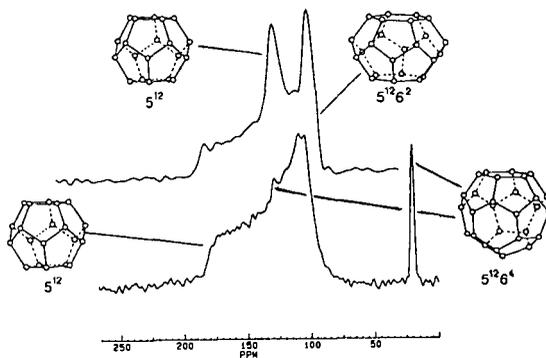


Figure 4. ^{13}C NMR spectrum for a str.H hydrate of CO_2 and 2,2 dimethyl butane. There is a small amount of str. I CO_2 hydrate present also. This spectrum does show liquid and gaseous CO_2 as a sharp line in the centre of the spectrum, as it was not recorded with a cross-polarization technique. The ^{13}C tensor pattern is axially symmetric for the $4^3 5^6 3$ (D') cage, and is a general tensor pattern for the low symmetry 5^{12} (D) cage.

