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Double clathrate hydrates with helium and hydrogen

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Double cubic structure II clathrate hydrates of tetrahydrofuran (THF) with helium (space group Fd3m, a = 17.155(5) Å, 120 K) or hydrogen and those of hexafluorophosphoric acid with hydrogen have been obtained. These hydrates are solid solutions due to the variable degree of the filling of the small cavities by helium and hydrogen molecules. The degree of the filling of the small cavities of the hydrate of THF by helium at 3.5 kbar is 24.5%; hydrogen can occupy 100% of the cavities, and at 7.0 kbar it is possible for two molecules to be accommodated in the small cavity.

INTRODUCTION

It is well known that clathrate hydrates of cubic structure II (CS-II) are stabilized by the introduction of an additional component, whose molecules can be accommodated either only in the small D-cavity (pentagonaldodecahedra) (e.g., H_2S^1), or in the four adjacent small D-cavities ($[(C_3H_7)_4N^+]^2$), the main guest molecules occupying the large 16-hedral cavities. On the other hand, small molecules, like argon, krypton, nitrogen, and oxygen, can form CS-II hydrates themselves, filling both the large and the small cavities.[3,4] Double clathrate hydrates obtained in this way are usually iskhoric solid solutions[5] formed due to the variable degree of the filling of the D-cavities by the molecules of an additional component.

In this study we have attempted to use the smallest molecules, helium and hydrogen, for the stabilization of CS-II hydrates.

RESULTS AND DISCUSSION

The very first experiment on using helium to stabilize a cubic structure II (CS-II) hydrate with tetrahydrofuran (THF) revealed that helium could occupy the small D-cavities, one volume of the hydrate absorbing 31 volumes of helium at 3.5 kbar (Table 1). The degree of filling the small cavities was 24.5%, and the stoichiometry of the hydrate formed was $THF.0.98He.17H_2O$. During the experiments on the decomposition of the hydrate and the determination of the amount of the absorbed helium temperature was gradually raised from 120 K, at the beginning of the experiment, to the hydrate melting point, at 5 degree/minute. It was noticed that the resulting hydrate practically did not give off helium up to 190 K. The amount of helium evolved increased gradually with the increase in temperature and achieved its maximum at 245 K. About 97% per cent of helium evolved at this temperature. The remaining helium gradually evolved until the hydrate melted completely at 278 K.

A single crystal X-ray study revealed the formation of the CS-II hydrate: space group Fd3m, Z = 8, a = 17.155(5) Å at 120 K. It is to be noted that the single crystals were taken from the sample of the composition $THF.7H_2O$, where at a pressure of 3.5 kbar in the absence of helium the hydrate of the composition $THF.7H_2O$ would have to be formed (presumably, cubic structure I (CS-I)[6,7]). The formation of the CS-II hydrate under these conditions shows that even the partial filling of the small cavities (1 of every 4) causes the expansion of its existence range to 3.5 kbar. However, further pressure increase results in the decomposition of the hydrate. At 7 kbar only 10.5 volumes of helium are absorbed. The double hydrate with helium obtained under these conditions is somewhat more stable; a noticeable release of helium at 1 atm was observed at 200 K. It is possible that at this pressure a CS-I hydrate forms; the small D-cavities in its structure are isolated from one another, and this may hinder the release of helium or some other hydrate

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Table 1 Data on the formation of double hydrates with helium and hydrogen

Main guest*	Auxiliary component	Pressure kbar	Temperature of the beginning of the decomposition, K (1 atm)	Ratio of the volume of the included gas to the volume of the hydrate (293 K)	Coefficient of filling of the small cavities
THF	He	3.5	190	31.0	24.5
THF	He	7.0	220	10.5	–
THF	H_2	3.5	210	119	91.0
THF	H_2	7.0	210	154	121**
HPF_6	H_2	3.5	200	42.1	33.3
HPF_6	H_2	7.0	200	124	98.2**

* Solutions of the composition $THF \cdot 17H_2O$ and $HPF_6.17H_2O$ were used

** Without considering hydrogen evolving during the high pressure plant disassembling.

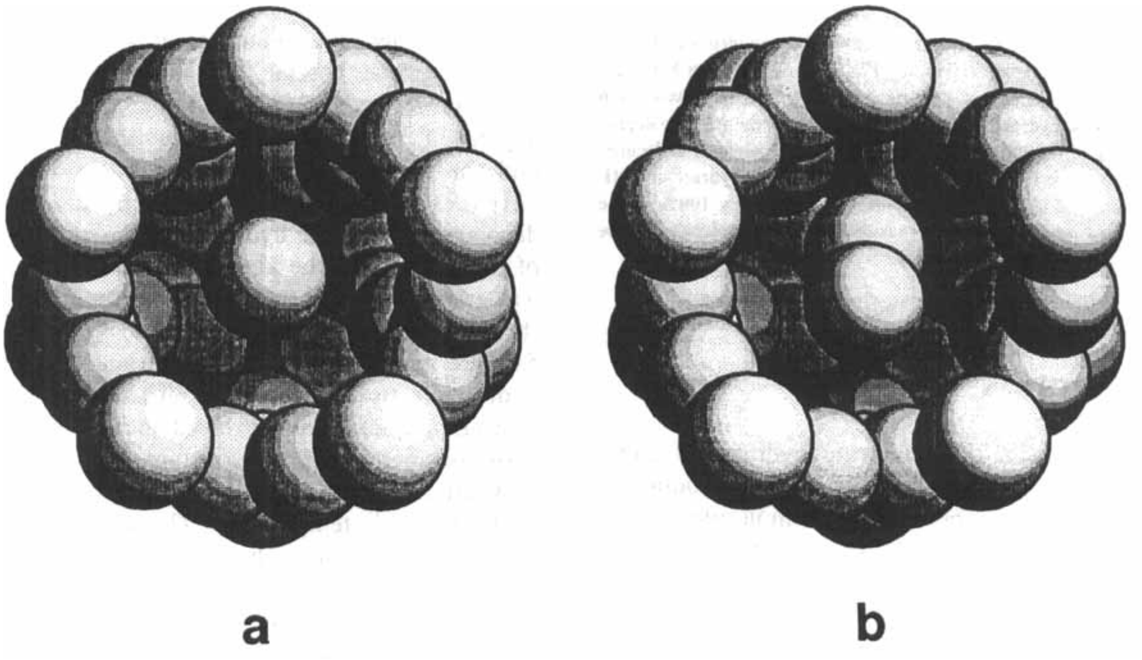

Figure 1 Helium (a) and hydrogen (b) molecules in the small D-cavity.

with the cavities smaller than pentagonaldodecahedra (which hold helium molecules stronger) may form.

A double hydrate was also obtained when hydrogen was used as an auxiliary component (Table 1). At a pressure of 3.5 kbar the $THF.17H_2O$ hydrate absorbs 119 volumes of hydrogen which corresponds to 91% filling of the small cavities and a stoichiometry of the resulting hydrate $THF.3.64H_2.17\ H_2O$. Such a high degree of filling of the small cavities by H_2 and the fact that the dimensions of the small D-cavity (d = 5.2 Å) are greater than those of H_2 (Fig 1) suggested that further increase of pressure would cause the increase of the degree of filling and the inclusion of the second H_2 into the D-cavity. To test this hypothesis the pressure was increased to 7 kbar. The results showed that a much larger volume of H_2 was absorbed at this pressure. After cooling to 180 K and disassembling the high pressure plant, the ampule with the sample was cooled to liquid nitrogen temperature. A vigorous escape of hydrogen was observed even at this temperature. The ampule with the sample was placed into a vessel for measurement of the volume of the escaping gas. 33 volumes of H_2 evolved at this temperature. Then the evoluation of H_2 stopped; it resumed at 210 K. During the second stage 121 volumes of H_2 evolved which corresponds to 96% filling of the small cavities. Taking account of the velocity of the hydrate decomposition, a rough extrapolation to the point of time at which the high pressure plant disassembling started leads one to the conclusion that the total volume of H_2 evolved was close to 250 volumes, and the filling degree was about 200%.

Similar results were obtained with HPF_6 as the main guest (Table 1). However, in this case at a pressure of 3.5 kbar, 42.1 volumes of H_2 was absorbed which corresponds to 33.3% filling of the D-cavities. The pressure increase of H_2 to 7 kbar resulted in the increase of the filling degree to 98%. The lower filling degree of the hydrate $HPF_6.17H_2O$ cavities might be due to the formation, in the case of the HPF_6 hydrate, of a water-cation host framework, which seems to be less favourable for the inclusion of neutral H_2 molecules.

EXPERIMENTAL

Gaseous helium and hydrogen (99.99%), distilled water, tetrahydrofuran (p.a.) distilled and freed from peroxides, and hexafluorophosphoric acid (60% wt. Aldrich) were used for the experiments. The experiments were carried out on a plant of the piston-cylinder type allowing pressure increase up to 10 kbar, and the needed pressure was created by the gases themselves. The solution to be studied was placed into a polyethylene ampule 10 mm in diameter with a cover having many small openings. The mass of the solution was about 0.5 g.

After the required gas pressure was set in the system, the temperature was lowered to 268 K and maintained fluctuating between −10° and +10° for 5 hours, allowing the hydrate formed to melt to a certain degree and to form again. After 5 hours, the temperature was lowered to 180 K; the high pressure plant was disassembled, and the ampule with the sample studied was cooled to the liquid nitrogen temperature. Then the single crystals were selected and withdrawn from the ampule at 120 K and placed into a Lindemann-glass capillary for X-ray analysis. X-ray single crystal intensity data were measured by using an Enraf-Nonius CAD-4 difractometer (120 K, CuKα, graphite monochromater). Experiments aimed at the determination of the volume of the evolving gas were carried out at atmospheric pressure and at the gas temperature 293 K. Blank experiments have also been carried out, and the volume of the gas evolved was 1 mL.

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