ORIGINAL ARTICLE

High-pressure clathrate hydrate of acetone

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Abstract X-ray diffraction study of quenched sample of acetone clathrate hydrate synthesized at 0.8 GPa was carried out. It was shown that the host frameworks of the hydrate comprise uniform cavities which are similar to that of recently characterized structure of high-pressure tetrahydrofurane hydrate. The unique peculiarity of investigated hydrate is decrease in the crystallographic symmetry of the hydrate arising from ordering in guest subsystem.

Keywords Clathrate hydrate · Acetone · High pressure · Stereohedra · Symmetry reduction

Introduction

Clathrate hydrates are inclusion compounds in which the host framework is formed by hydrogen-bonded water molecules, while the guest molecules (a gas or a readily volatile liquid) are situated in the polyhedral cavities of this framework [1]. In clathrate hydrates existing at relatively low pressure (cubic structures I and II, structure H), host frameworks contain several types of polyhedral cavities differing in size, whereas recently discovered host frameworks of high-pressure clathrate hydrates comprise uniform cavities [2–4]. Modeling of possible topological types of such polyhedral frameworks [5, 6] revealed the existence of some space-filling polyhedral cavities with the number of faces exceeding 13 (there are 23 packings of 14-hedra). It is necessary to gain structural information on high-pressure hydrates to determine the abundance and structural diversity of the new structural class of hydrate inclusion compounds. The progress in this branch of structural chemistry of clathrate hydrates can become an important impetus for some other areas like structural chemistry of clathrasils [7] and so-called semiconductor clathrates [8].

It seems probable that an acetone hydrate existing at highest pressures belongs to the mentioned above type of hydrates with the host framework comprised of uniform cavities. The phase diagram of acetone–water system was considered in ref. [9]. It was shown that three hydrates exist in the system at pressures below 1 GPa. The hydrate of cubic structure II is stable at atmospheric pressure [10]; it exists up to the pressure of 165 MPa. Another hydrate (h_2, reported stoichiometry: $(CH_3)_2CO*7H_2O$, assumed structure: CS-I) occurs within pressure range 100–315 MPa. Finally, the third hydrate (h_3, reported stoichiometry: $(CH_3)_2CO*5H_2O$) appears in the system at a pressure about 120 MPa; this means that all hydrate phases are stable within 120-165 MPa. In the present work we report on the data of X-ray structural investigation of h_3 acetone hydrate.

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Experimental

Acetone hydrate h_3 was obtained by pressurizing approximately 5 mL of water–acetone mixture (molar ratio 6:1) to the pressure of 800 MPa at room temperature. After 24 h

the high-pressure apparatus was frozen to the liquid nitrogen temperature, and the quenched hydrate sample was taken out. Further manipulations with the hydrate were carried out at the liquid nitrogen temperature; the time span from sample extraction to the X-ray experiment did not exceed 2 h. The powder diffraction patterns were recorded using the synchrotron radiation at the 4th channel of VEPP-3 storage ring (Institute of Nuclear Physics, SB RAS, Novosibirsk) [11]. The wavelength of the radiation involved was 0.3675 Å. Series of powder diffraction patterns of the sample was taken at temperatures ranging from 78 K to room temperature. Sample heating rate was varied within the range 2–3°/min, total duration of an experiment was one hour and a half. The diffraction patterns were registered with an ImagePlate MAR-345 detector. Integration was carried out using FIT2D program [12], the distance from the sample to the detector was determined using the diffraction patterns of a reference substance (NaCl). Location of reflections, indexing trials, refinement of unit cell parameters and development of model diffraction patterns were carried out with the programs Full-Prof [13] and XLAT [14].

Fig. 1 (**a**) Experimental powder diffraction patterns of the quenched acetone hydrate sample at T = 85 K; Diffraction patterns for space groups P2$_1$/n11 (**b**) and P2$_1$2$_1$2$_1$ (**c**) simulated in assumption of the position of acetone molecule in the cavity shown in Fig. 2

Results and discussion

The experimental X-ray diffraction pattern of a quenched sample of the h$_3$ acetone hydrate is shown in Fig. 1a. Indexing the experimental diffraction patterns of the hydrate yielded a probable unit cell with parameters close to those of the orthorhombic unit cell of the tetrahydrofuran clathrate hydrate THF · 6H$_2$O studied by us earlier [3] (Fig. 2, structural type: RS-III, Pnma, a = 12.54 Å, b = 11.44 Å, c = 6.60 Å at T = 293 K, P = 800 MPa), the host framework is composed of congruent 14-faced cavities having four quadrangular faces, four pentagonal and six hexagonal ones). However, the presence of the reflection with 2θ = 2.498° (corresponding to the 1 1 0 reflection of the above-mentioned unit cell metrics) in our diffraction patterns points to decreased symmetry of the hydrate as compared to the symmetry of the idealized RS-III hydrate framework. The most probable assumption is that the decrease in the symmetry of the hydrate occurs due to symmetry violation at the position occupied by the guest molecule (in the idealized RS-III framework and in THF · 6H$_2$O hydrate—the mirror plane symmetry), the symmetrical identity of the cavities being preserved. Probing possible spatial arrangement of the acetone molecule in the cavity under consideration, carried out with EENY program (S. Motherwell, *Potential Energy Program*, University Chemical Laboratory, Cambridge (UK)), demonstrated that the most favorable orientations of the
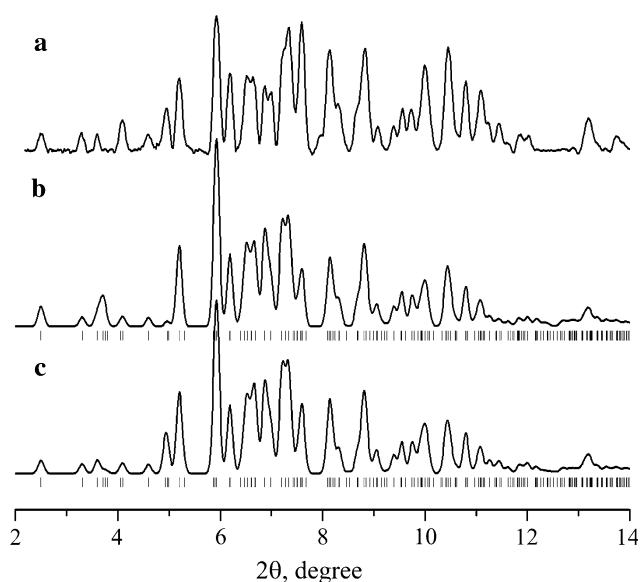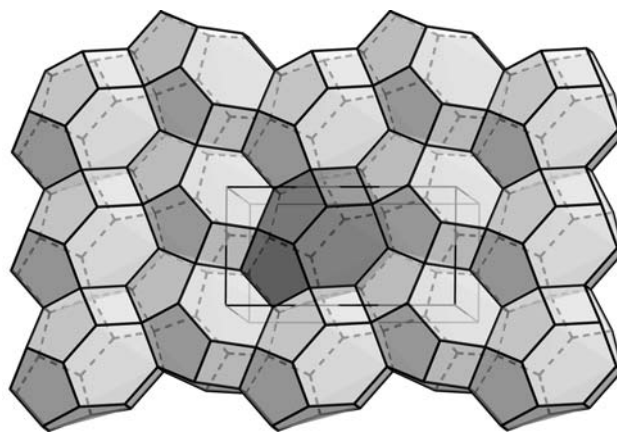

Fig. 2 A layer of symmetrically equivalent polyhedra. The whole RS-III host framework may be represented as close pack of the layers

acetone molecule in the cavity indeed do reduce its maximum symmetry (Fig. 3).

There are four subgroups of the Pnma group preserving the symmetrical equivalence of the cavities: Pn2$_1$a, P112$_1$/a, P2$_1$/n11, P2$_1$2$_1$2$_1$ (the directions of axes of the unit cell are retained). The first two subgroups should be ruled out due to the absence of the reflection 1 1 0. The calculated diffraction patterns for the structures in the two remaining groups with the optimized position of the acetone molecule are shown in Fig. 1b, c. The largest similarity to the experimental diffraction patterns (especially within the angle range 2θ = 4,930–5.997°, reflections 0 2 1, 2 1 1 and 2 2 0) is observed for the case of the P2$_1$2$_1$2$_1$ group; poor
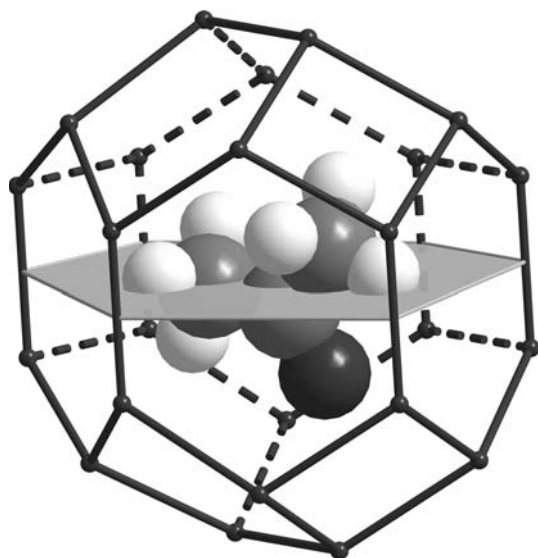
Fig. 3 A model of the arrangement of acetone molecule in the cavity of the RS-III framework distorting the symmetry of the mirror plane of the cavity

agreement in intensity of the strongest diffraction peak comes from the features of the integration procedure (the presence of overexposed spots in the diffraction ring). Though the quality of the experimental powder diffraction patterns precludes from refinement of the structure by the Rietveld method, the similarity between the experimental

patterns and the one simulated for the acetone hydrate with RS-III framework and the symmetry decreased to $P2_12_12_1$ (Fig. 1a, c) allows us to consider this model as the most plausible one. The absence of ice and solid acetone reflections in the experimental diffraction patterns confirms the validity of 6:1 water–acetone ratio following from the structural model suggested.

The final refinement of the unit cell parameters gives $a = 12.76 \pm 0.01$ Å, $b = 11.21 \pm 0.01$ Å, $c = 6.587 \pm 0.002$ Å, $V = 942.2 \pm 0.9$ Å^3 ($T = 85$ K, Table 1). Processing of the entire series of the diffraction patterns taken on sample warming shows that the decomposition of the quenched hydrate sample h_3 at atmospheric pressure appears at 178 K (Table 2). At higher temperatures only the reflections corresponding to the expected clathrate hydrate of CS-II are observed in the diffraction patterns; this fact makes it possible to assume that the h_3 hydrate decomposes into h_1 and a liquid phase rich with acetone.

Thus, in the present work we pioneered the determination of the crystal structure of acetone hydrate existing at high pressure. The true composition of this hydrate resulting from the suggested crystal structure is $(CH_3)_2CO \cdot 6H_2O$. The structure is very similar to that of the tetrahydrofuran hydrate; however, this hydrate exemplifies a novel phenomenon unprecedented for the low pressure gas hydrates: the symmetry reduction of the host framework as a consequence of ordering in the guest subsystem.

Table 1 A comparison of the main calculated and observed reflections for the quenched high-pressure acetone hydrate within the range $2\theta = 2.5$–$7.0°$ ($T = 85$ K)

	h	k	l	d_{calc}	d_{obs}		h	k	l	d_{calc}	d_{obs}		h	k	l	d_{calc}	d_{obs}
	1	1	0	8.420	8.421		2	3	0	3.223	-//-		2	2	2	2.594	-//-
*	2	0	0	6.382	6.402		4	0	0	3.191			3	3	1	2.582	
*	1	0	1	5.854	5.854		1	0	2	3.189			2	4	0	2.565	
	0	2	0	5.602	-		0	1	2	3.160	3.163		3	1	2	2.537	2.534
	1	1	1	5.188	5.152		1	3	1	3.148			1	4	1	2.527	
	1	2	0	5.129		*	1	1	2	3.067	3.067		4	3	0	2.426	2.432
*	2	0	1	4.584	4.585	*	3	2	1	3.013	3.013		1	3	2	2.425	
	0	2	1	4.267	4.261		2	0	2	2.927	2.925		2	4	1	2.390	2.388
	2	1	1	4.242			2	3	1	2.895			5	0	1	2.380	
	1	2	1	4.047	4.052		4	0	1	2.872	2.873		3	2	2	2.362	2.321
	3	1	0	3.978			0	2	2	2.839			5	1	1	2.328	
	3	0	1	3.574	3.553		0	4	0	2.801	2.775	*	4	1	2	2.245	2.245
	2	2	1	3.547			4	1	1	2.782		*	3	4	1	2.205	2.205
*	3	1	1	3.405	3.403		4	2	0	2.773			1	0	3	2.164	2.165
	0	0	2	3.294	3.230		1	2	2	2.772			0	1	3	2.155	
	0	3	1	3.249			3	0	2	2.605	2.590						

An asterisks mark the reflections used to calculate the unit cell parameters with the XLAT program

Table 2 Temperature dependence of orthorhombic unit cell parameters of quenched h$_3$ hydrate obtained using XLAT program. Unit cell parameters for temperature region $T = 85–159$ K were refined over eight reflections (Table 1, reflections marked by asterisk). Unit cell parameters for $T = 178$ K were refined over seven reflections (Table 1, reflections marked by asterisk except 3 1 1 reflection)

T, K	a, Å	b, Å	c, Å	V, Å^3
85	12.76 ± 0.01	11.21 ± 0.01	6.587 ± 0.002	942.2 ± 0.9
112	12.76 ± 0.02	11.23 ± 0.02	6.605 ± 0.005	945.9 ± 2.4
138	12.78 ± 0.03	11.24 ± 0.02	6.619 ± 0.007	951.3 ± 2.8
159	12.82 ± 0.03	11.26 ± 0.01	6.621 ± 0.009	955.5 ± 3.0
178	12.81 ± 0.06	11.30 ± 0.04	6.616 ± 0.013	957.8 ± 5.6

References

1. Sloan, E.D. (ed.): Clathrate Hydrates Of Natural Gases, 2nd edn. Marcel Dekker, New-York (1998).
2. Manakov, A.Yu., Voronin, V.I., Kurnosov, A.V., Teplykh, A.E., Komarov, V.Yu., Dyadin, Yu.A.: Structural Investigations of Argon Hydrates at Pressures up to 10 kbar. J. Inclusion Phenom. **48**, 11–18 (2004).
3. Kurnosov, A.V., Komarov, V.Yu., Voronin, V.I., Teplykh, A.E., Manakov, A.Yu.: New clathrate structure: high-pressure tetrahydrofuran hydrate with one type of cavity. Angew. Chem. Int. Ed. **43**, 2922–2924 (2004).
4. Loveday, J.S., Nelmes, R.J., Guthrie, M., Belmonte, S.A., Allan, D.R., Klug, D.D., Tse, J.S., Handa, Y.P.: Stable methane hydrate above 2 GPa and the source of Titan's atmospheric methane. Nature **410**, 661–663 (2001).
5. Komarov, V.Yu., Solodovnikov, S.F., Kurnosov, A.V., Kosyakov, V.I., Manakov, A.Yu.: Design of tetrahedral frameworks as layered packings of uniform polyhedral cavities. J. Struct. Chem. **46**, S181–S187 (2005) (translated from Russian *Zh. Strukt. Khim.* 46, 177 (2005)).
6. Delgado-Friedrichs, O., O'Keeffe, M.: Isohedral simple tilings: binodal and by tiles with 16 faces. Acta Cryst. **A61**, 358–362 (2005).
7. Gies, H., Marler, B.: Crystalline Microporous Silicas As Host-Guest Systems. In: MacNicol, D.D., Toda, F., Bishop, R. (eds.) Comprehensive Supramolecular Chemistry, vol. 6, pp.851–883, Pergamon Press, Oxford (1996).
8. Kovnir, K.A., Shevelkov, A.V.: Semiconducting clathrates: synthesis, structure and properties. Russ. Chem. Rev. **73**, 923–938 (2004) (translated from Russian Usp.Khim. **73**, 999 (2004)).
9. Dyadin, Yu.A., Bondaryuk, I.V., Zhurko, F.V.: Clathrate Hydrates at High Pressures. In: Atwood, J.L., Davies, J.E.D., MacNicol, D.D. (eds.) Inclusion Compounds, vol. 5, pp.213–275. Oxford University Press, Oxford (1991) .
10. Quist, A.S., Frank, H.S.: Ice VIII-an acetone hydrate? J. Phys. Chem. **65**, 560–562 (1961).
11. Ancharov, A.I., Manakov, A.Yu., Mezentsev, N.A., Tolochko, B.P., Sheromov, M.A., Tsukanov, V.M.: A new station at 4th beamline of the VEPP-3 storage ring. Nucl. Instrum. Methods Phys. Res. **A470**, 80–83 (2001).
12. Hammersley, A.P.: Synchrotron Radiat. News **2**, 24 (1989); Program FIT2D under: http://www.esrf.fr.
13. Rodriguez-Carvajal, J.: FULLPROF: A Program for Rietveld Refinement and Pattern Matching Analysis. Proc. of the Satellite Meeting on Powder Diffraction of the XV IUCr Congress, 127 (1990)
14. Rupp, B.: XLAT-least Squares Refinement of Cell Constants. Scr. Metall. **22**, 69–92 (1988).