The structure of the ionic clathrate hydrate of tetrabutylammonium valerate $(C_4H_9)_4NC_4H_9CO_2\cdot39.8H_2O$†

Tatyana Rodionova,*[a] Vladislav Komarov,[a] Janusz Lipkowski[b] and Natalia Kuratieva[a]

Received (in Montpellier, France) 31st July 2009, Accepted 17th November 2009
First published as an Advance Article on the web 19th January 2010
DOI: 10.1039/b9nj00530g

For the first time the detailed crystal structure of the ionic clathrate hydrate of tetrabutylammonium valerate $(C_4H_9)_4NC_4H_9CO_2\cdot39.8H_2O$ has been determined by single crystal X-ray analysis at 150 K. The idealized water–anion host framework consists of five-compartment polyhedral cavities 4T·P and small D cavities. Butyl chains of the cation and the anion of $(C_4H_9)_4NC_4H_9CO_2$ are included in the five-compartment cavities with displacement of two "inner" host water molecules. The inclusion of the guest entities leads to the distortion of D-cavities which are partially filled by additional "guest" water molecules. The other D-cages are empty. The structure exhibits significant disordering. The adequate model of disordering and inclusion mode of the guest moieties have been obtained. Special features of the crystal structures of ionic clathrate hydrates of tetraalkylammonium carboxylates are discussed.

Introduction

In the crystal structure of polyhydrates of tetrabutyl- and tetraisopentylammonium carboxylates, water molecules together with the oxygen atoms of the carboxylate anions form the polyhedral water–anionic host framework through hydrogen-bonding (hydrophilic hydration). Hydrophobic parts of cations and anions are incorporated in polyhedral cavities of the water–anionic framework so that distances between the atoms of hydrophobic groups and water framework are not less than a sum of their van der Waals radii (hydrophobic hydration).[1–3] These compounds belong to the ionic clathrate hydrates (according to Jeffrey's classification[1]) and their host lattices are structurally related to those of gas hydrates. The latter have been subjected to comprehensive study, particularly in the last forty years subsequent to discovery of vast amount of methane in hydrated form *in situ* both in marine sediments and permafrost regions (estimates of methane volume in gas hydrates deposits vary significantly, but even according to a conservative estimate, $\sim6 \times 10^{15}$ m^3, it is two orders of magnitude greater than that found in conventional assured gas resources).[4–6]

The ionic clathrate hydrates of tetraalkylammonium salts have been extensively investigated in the last decade as potentially available for manifold applications. The tetrabutylammonium bromide hydrates attract attention as materials for cold storage and transportation since (1) their latent heat of phase changes is sufficient for cold storage, and (2) their formation/decomposition temperatures lie in the range of 0–12 °C (depending on the salt concentration), and in addition, (3) they form a slurry, that can be transported directly through a pipeline.[7–10] The capability of ionic clathrate hydrates to incorporate small gas molecules such as hydrogen,[11–16] methane,[11,16–19] nitrogen,[11,17] hydrogen sulfide,[17] carbon dioxide[11,16,20] due to existence of empty cavities in their crystal structures opens up possibilities to use them for storage, transportation and separation of gases.[16–18,21] Very recently tetrabutylammonium borohydride clathrate hydrate was demonstrated to include molecular hydrogen in vacant cavities of crystal structure and thus can be used as a hybrid material for hydrogen storage (H_2 releases under clathrate decomposition and additional hydrogen is produced *via* a hydrolysis reaction between the water host molecules and borohydride anions).[22]

There is a connection between the hydration of hydrophobic groups, hydration of biomolecules, and structure of liquids. There are evidences of the formation of clathrate-like ordered water structures around biomolecules.[23] The results of the studies of aqueous solutions of nonelectrolytes are often interpreted in the frame of clathrate-like models of liquid water.[24] From this point of view the investigations of ionic clathrate hydrate crystal structures are important since they enable creation of a base for modeling of structures of aqueous solutions of organic compounds and structures of hydration shells of biomolecules.

Many of ionic clathrate hydrates of tetrabutylammonium carboxylates have been analysed by phase diagram studies, and/or crystallographic data,[25–30] but their crystal structures are still unknown. This can be mainly explained by the fact that structure solution of such compounds is complicated by a low scattered intensity due to the lack of heavy atoms, significant positional and oriental disordering, and pseudosymmetry of host framework.[3,30–32]

Previous studies showed that several ionic clathrate hydrates are formed in tetrabutylammonium valerate $(C_4H_9)_4NC_4H_9CO_2$–H_2O binary system (Table 1).[25–27,30] The T,X-phase diagram of this system is very complicated. It was scrutinized in ref. 25 by

---

[a] *Nikolaev Institute of Inorganic Chemistry, Siberian Branch of RAS, 3, Lavrentyeva Ave., Novosibirsk, 630090, Russia. E-mail: tvr@niic.nsc.ru; Tel: +7 383 330 53 46; Fax: +7 383 94 89*
[b] *Institute of Physical Chemistry, Polish Academy of Sciences, 44, Kasprzaka, Warsaw, 01 244, Poland*

† CCDC reference number 693261. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b9nj00530g

Table 1 Hydrates numbers, m.p. and crystal data for ionic clathrate hydrates of tetrabutylammonium valerate

Hydrate number	M.p./°C	Bravais lattice, Laue symmetry	Unit cell dimensions/Å *a*	*c*	*Z*	References
39.7	10.2	*P*, 4/*mmm*	23.5	12.3	4	25,26
40 (1)	10.6	—	—	—	—	27
39.5 (1)	—	4/*mmm*	23.59	12.43	4	30
—	—	*m*-3*m*	12.31	—	—	30
35	11.2	—	—	—	—	25,26
35	9.6[a]	—	—	—	—	25,26
35	8.9[a]	—	—	—	—	25,26
31.6(3)	10.5[a]	*P*, *m*-3*m*	12.4(1)	—	1.33	25,26
27	9.4[a]	—	—	—	—	25,26

[a] Metastable phase.

differential thermal analysis and the existence of six distinct polyhydrates was revealed in the clathrate formation region. One polyhydrate was stable and the other five were metastable. Crystallographic data (crystal symmetry and unit cell metrics) were obtained only for two polyhydrates with hydration numbers 39.7 and 31.6 and they were ascribed to tetragonal structure-I (TS-I) and cubic structure-I (CS–I), respectively, but detailed crystal structures remained unknown.

In this paper, for the first time the structure of the tetragonal ionic clathrate hydrate of the tetrabutylammonium valerate $(C_4H_9)_4NC_4H_9CO_2{\cdot}39.8H_2O$ is described. The hydrate number obtained from the structure determination (39.8) is in close agreement with analytical data (39.7).

Experimental

An aqueous solution of tetrabutylammonium valerate was prepared by neutralizing an aqueous solution of tetrabutylammonium hydroxide (10 wt%, "pure" grade) with an aqueous solution of valeric acid (~70 wt.%, "pure" grade). The solution obtained was cooled (+1–+3 °C) until crystalline specimens were produced. The crystals obtained were collected by filtration, and then recrystallized twice in the same way. The polyhydrate crystals were grown as transparent tetragonal prisms from ~20 wt% salt solution at a temperature between +2–+3 °C. For analytical determination of the hydrate composition a portion of crystals was separated out from the above solution and quickly dried between two sheets of filter paper. The concentration of the tetrabutylammonium valerate was determined by measuring the amount of tetrabutylammonium cation by potentiometric titration with a sodium tetraphenylborate solution and ion-selective electrode. The stoichiometry of the compound corresponded to the composition $(C_4H_9)_4NC_4H_9CO_2{\cdot}(39.7 \pm 0.1)H_2O$. The m.p. was determined in a thin-walled glass capillary and was found to be 11.3 °C.

Two X-ray data collection experiments were performed at 150 K. In the first attempt rather sizeable single crystal 0.7 × 0.7 × 1.0 mm was selected. The diffraction data were collected with a Bruker X8 APEX diffractometer equipped with CCD detector and Mo-Kα radiation source.[33] Full sphere was collected using φ and ω scan mode over a 2θ range of 2.46°–50.0° with data completeness over 99%. The structure was solved by direct methods and refined by full-matrix least-squares on $|F|^2$ using SHELXTL programs set in $P4_2/mnm$. Thermal parameters of ordered water oxygen (O0x) were refined anisotropically. Oxygen atoms of water molecules at essentially split positions (O1x, O2x, O3x) were refined isotropically with equal displacement parameters for the atoms at the same site. Positions of water hydrogens were not determined. Non-hydrogen atoms of the guest species are refined isotropically as disordered over four sites with restraints on interatomic distances (parameters of restraints are 1.52(5) Å for C–C and C–N bonds, 1.25(5) Å for carboxylate C–O bond; 2.49(10) Å for C–X–C and C–X–N, 2.38(10) Å for O–C–C, 2.20(10) Å for O–C–O angle distances). The decreasing of positional disordering is most likely in the space group of lower symmetry $P4_2/m$. However a structure refinement in this space group with using of appropriate twinning matrix did not lead to a less-disordered system. Coordinates of hydrogen atoms of the tetrabutylammonium cation were determined geometrically. The final cycles of the structure refinement were carried out on the reduced data set with 2θ range of 5.52°–39.96° to diminish the influence of missing water hydrogen atoms on resulting *R*-values (R = 6.72%, wR = 20.12% for 1575 data with $F_0 > 4\sigma(F_0)$). In spite of data set reduction, the refinement process remained stable and no essential changes in the structure model were observed.

Another single crystal experiment with a crystal sized 0.2 × 0.2 × 0.3 mm was carried out to ensure that the quality of the X-ray data has not been affected by the large size of the crystal studied. The diffraction data were collected with a Nonius Kappa CCD diffractometer using Mo-Kα radiation.[34] A quarter sphere was collected in φ and ω scan mode over 2θ range of 5.82°–49.42°, data completeness 61.9%. The structure refinement was carried out as described above to converge to R = 7.19%, wR = 21.66% for 1614 data with $F_0 > 4\sigma(F_0)$.

Final refinement was performed with the use of combined data sets from the two independent data collections. The batch scale factors were determined using refinement procedures of the SHELXL-97 programme, then the both sets were merged into a combined single reflection file. This procedure did not reveal any special characteristic of the component data sets but is a convincing proof the large crystal used for the first data collection did not provoke any systematic bias of the resulted X-ray structure.

Crystal data and structure refinement information are listed in Table 2.

Table 2 Crystal data and structure refinement for $(C_4H_9)_4N\ C_4H_9CO_2{\cdot}39.8H_2O$

Chemical formula	$C_{21}\ H_{124.6}\ N\ O_{41.8}$
Formula weight	1060.87
Temperature	150(2) K
Crystal system, space group	tetragonal, $P4_2/mnm$
Unit cell dimension:	
a	23.322(1) Å
c	12.278(1) Å
Volume	6678.2(7) $Å^3$
Z, calculated density	4, 1.055 Mg m^{-3}
$F(000)$	2368
Crystal size	1.0 × 0.7 × 0.7, 0.2 × 0.2 × 0.3 mm^3
θ range for data collection	2.76 to 19.98°
Index ranges	
$h_{\min}$, $h_{\max}$	0, 15
$k_{\min}$, $k_{\max}$	0, 22
$l_{\min}$, $l_{\max}$	0, 11
Unique reflections	1721
Data/restraints/parameters	1721/46/205
Goodness of fit on F^2	1.108
R-values [$I > 2s\ (I)$]	$R = 0.0668$, w$R = 0.2069$
R-values (for all data)	$R = 0.0692$, w$R = 0.2098$
Largest diff. peak and hole	0.278 and −0.203 e $Å^{-3}$

Single crystal X-ray diffraction data have been deposited with the Cambridge Crystallographic Data Centre, deposition number CCDC 693261†.

Results and discussion

For hydrate structures, it is convenient to describe an idealized host water framework admitting that all vertices of the polyhedra are water oxygens and all the edges are equal, and then to discuss distortions appearing on guest molecules inclusion.

The host framework of the studied hydrate can be considered as a distortion of the idealized water framework of the tetragonal structure-I (TS-I) with space group symmetry $P4_2/mnm$ and unit cell dimensions $a \approx 23$ Å, $c \approx 12$ Å. The idealized host water lattice of TS-I can be described as a close packing of polyhedral cavities (D, T, P cavities) composed of hydrogen-bonded water molecules. D, T, P cavities are pentagonal dodecahedron (5^{12}), tetrakaidecahedron ($5^{12}6^2$), and pentakaidecahedron ($5^{12}6^3$), respectively. The ideal unit cell stoichiometry is $4P{\cdot}16T{\cdot}10D{\cdot}172H_2O$.[1] Thorough structure description reveals that the layers perpendicular to [001] direction consist of D^1 (Wyckoff position 8*i*), D^2(2*a*), T^1(8*i*) and P(4*f*) polyhedra (here and hereinafter the upper indices are used to denote symmetry-nonequivalent polyhedra), as shown in Fig. 1. The whole framework is constructed from these layers rotated by 90° relatively to one another, so that (1) three adjacent pentagonal faces of P cavity of one layer are shared with pentagonal faces of two D^1 and one D^2 cages of another layer, and (2) three adjacent pentagonal faces of T^1 cages of one layer are shared with pentagonal faces of two T^1 and one D^1 cages of another layer. Such arrangement also results in the formation of T^2 cavities in 8*j* position between the layers. Thus, the ideal unit cell composition can be described as $8T^1{\cdot}8T^24P{\cdot}8D^1{\cdot}2D^2{\cdot}172H_2O$.

Inclusion of tetrabutylammonium valerate induces distortions of the ideal water framework of TS-I. Five polyhedra are fused to form a larger five-compartment $2T^1{\cdot}2T^2{\cdot}P$ cavity with point symmetry *mm2* (Fig. 2a). In this cavity the vertices of the edge common to P, two T^2, and one T^1 polyhedra are not occupied by water molecules. The vertices of $2T^1{\cdot}2T^2{\cdot}P$ cavity can be classified into three types. Vertices of α- and β- types are four-connected oxygen atoms belonging to one (α-type) or two (β-type) of the five polyhedra, whereas γ-type vertices are three-connected oxygens belonging to three of the five polyhedra of this five-compartment cavity. The oxygen atoms of β- and γ-types are bonded only with oxygens within $2T^1{\cdot}2T^2{\cdot}P$ cavity, whereas one bond of α-type oxygens is directed outwards. Five-compartment $2T^1{\cdot}2T^2{\cdot}P$ cavity has six vertices of the γ-type. Two of them lie on the mirror plane and belong to one T^1 and two T^2 polyhedra (γ_1), whereas the other four occupy general positions and belong to P, T^1 and T^2 polyhedra (γ_2).

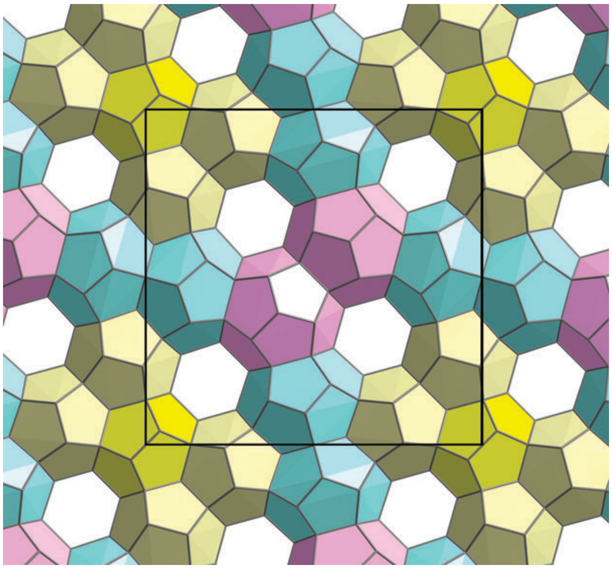

Fig. 1 The polyhedral layer perpendicular to the [001] direction. D^1, D^2, T^1, P cavities are marked with yellow, canary-yellow, blue, and lilac, respectively.

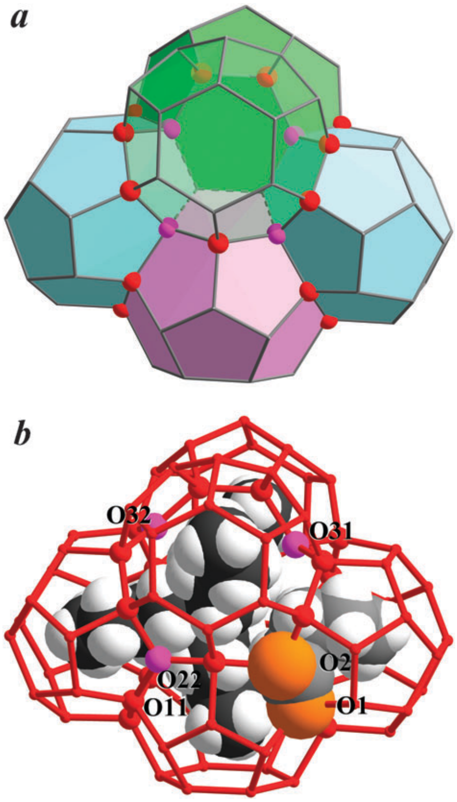

Fig. 2 The five-compartment $2T^1{\cdot}2T^2{\cdot}P$ cavity: (a) lilac and red balls are the oxygen atoms of γ- and β-types, respectively; (b) accommodation of tetrabutylammonium cation–valerate anion guest pair is shown in van der Waals radii.

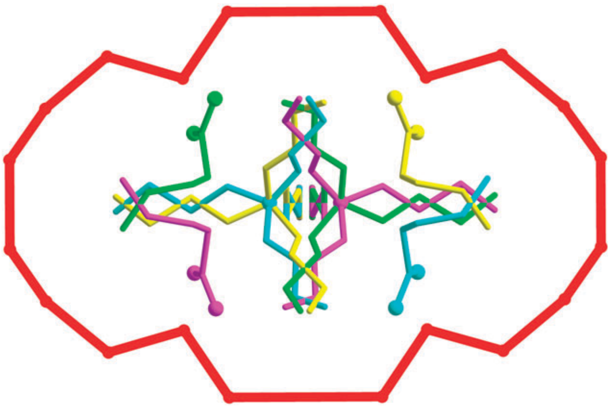

Fig. 3 The scheme of guest moieties disordering. Four different positions of guest butyl chains in 4TP five-compartment cavity are marked with yellow, lilac, blue, and green.

Table 3 The deviations of γ-type oxygen atoms from special planes through the three adjacent β-type oxygen atoms

Atom (γ)	Three adjacent atoms (β)	Distance to plane[a], Å
O2	O08[b], O0D, O1	−0.083(18)
O21	O08, O0D, O11	1.075(12)
O22	O08, O0D, O11	−0.239(15)
O23	O08, O0D, O11	0.498(13)
O31	O04, O04[c], O0C	0.862(9)
O32	O04, O04[b], O0C	0.174(9)

[a] Negative value for distance implies that atom and center of five-compartment cavity are arranged on opposite sides of plane. [b] Symmetry code: $1 - y$, $1 - x$, z; [c] Symmetry code: x, y, $-z$.

Table 4 Selected bond angles (°)

O08-O21-O0D	100.5(4)	O04-O31-O04[a]	112.3(3)
O08-O21-O11	109.1(4)	O04-031-O0C	110.4(2)
O0D-O21-O11	111.5(4)		
O08-O22-O0D	118.2(5)	O04-O32-O04[a]	121.0(3)
O08-O22-O11	116.7(4)	O04-032-O0C	118.9(1)
O0D-O22-O11	122.7(5)		
O08-O23-O0D	110.0(6)		
O08-O23-O11	118.3(6)		
O0D-O23-O11	121.9(5)		

O21, O22, O23, O31, O32 are γ-type oxygens.[a] Symmetry code: x, y, $-z$.

The cation–anion pairs of tetrabutylammonium valerate are located in these $2T^1{\cdot}2T^2{\cdot}P$ cavities (Fig. 2b). Four butyl chains of the cation are accommodated within P, T^1, and two T^2 polyhedra. The butyl chain of the anion is arranged in the remaining T^1 polyhedron. Incorporation of the oxygen atoms O2 and O1 of the valerate carboxyl in host framework results in replacement of the two adjacent water molecules (γ_2- and β-types) belonging to the P and T^1 compartments. Inclusion of guest particles breaks the symmetry of the cavity and results in statistical disordering in both guest and host subsystems. The guest species are disordered over four distinctly differing positions (Fig. 3). Disordering in the host framework leads to splitting positions of γ type water oxygens, and to elongated thermal ellipsoids of adjacent β type water oxygens (O04, O08, O0C, O0D). Inclusion of alkyl groups of the cation "squeezes out" O32 (γ_1) and O22, O23 (γ_2) water oxygens belonging to T^1 polyhedron of $2T^1{\cdot}2T^2{\cdot}P$ cavity (Table 3). Their resulting bond angles are significantly different from tetrahedral ones (Table 4). The surroundings of O31 (γ_1) and O21 (γ_2) of water molecules belonging to the T^1 cavity filled by the alkyl group of the anion are closer to the idealized framework structure.

Some D^1 cavities are filled by additional "guest" water molecules (O0E). It is likely that D^1 cavities can exist in two basic configurations (Fig. 4): (1) a slightly distorted one containing O21, O23, and O31 oxygen atoms; (2) a strongly distorted one containing O22, O32 atoms of water molecules and oxygen atoms of carboxyl group. In the latter case the "guest" water molecule O0E is surrounded by three adjacent atoms O22, O32, and O2 at the distances of hydrogen bonding.

If the D^1 cavities exist only in the two configurations described above and all strongly distorted D^1 cavities contain the "guest" water molecule, the occupancy of the O0E atom would be 50%. However, the experimentally observed s.o.f. is 40.6(16)%. That may be due to (1) refinement faults ("guest" water molecules disordered over several positions were refined as a single oxygen atom), and (2) the presence of unoccupied strongly distorted D^1 cavities or D^1 cavities with intermediate configuration. It should be noted that the proposed disordering model is not strict. Interatomic distances and angles in tetrabutylammonium valerate species significantly deviate

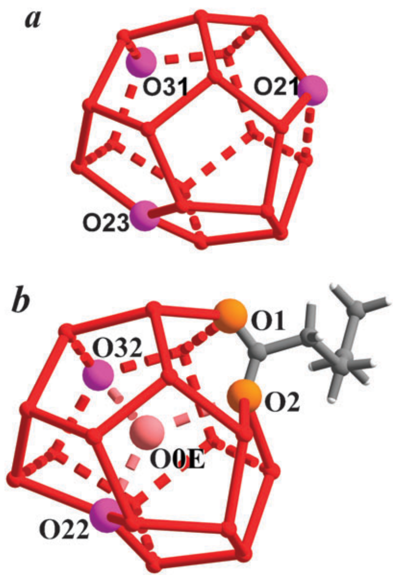

Fig. 4 The slightly (a) and strongly (b) distorted D^1 cavities. The oxygen atom of guest water molecule is marked with pink.

from the characteristic values. The tendency of shortened interatomic distances and increased bond angles can be attributed to determined positions resulting from averaging of some actual positions. The possibility of two close positions of the anion alkyl radical is suggested by the increased Uiso value for C01 as compared to the neighboring atoms. Structure refinement in anisotropic fitting reveals an elongated ellipsoid with principal rms atomic displacements 0.4431, 0.1203 and 0.0447. Taking into account that slight steric hindrance between the cation and the anion occurs only for the hydrogen atoms connected with C01, one may assume that each of these positions corresponds to one of two possible orientations of cation. In the host framework O···O hydrogen bonding distances mostly range from 2.73 to 2.86 Å. The longest (max. 2.93(1) Å) and the shortest (min. 2.51(1) Å) distances are observed for O04, O08, O0C, O0D, O0E oxygen atoms, which are the averaged for several positions. Each of the above mentioned oxygen atoms makes both the shortest and the longest bonds.

Hydrogen bond angles vary in a broad range (minimum value 84.1(1)° for O0C–O32–O0E angle, maximum value 156.5(3)° for O22–O0B–O2). However, there are several bond angles for each water molecule, except O0E, that correspond to the optimal range (105°–109.5°). This means that different orientations of water molecules have different binding energies. As a result, partially ordering of hydrogen atoms of the host framework must occur.

Indicative characteristics of the host water framework are the hydrogen bonds balance (Δ) and the hydrate number (h). Δ can be determined as a difference between a number of "donor" hydrogen atoms (d) and the number of lone electron pairs of oxygen atoms (b) within the range of hydrogen bonding normalized to one guest particle. Provided "donor" hydrogens belong only to the water molecules, d is equal $2h$. Omitting the "guest" water molecules, Δ and h can be calculated by the following way: (1) $h = N/Z = 172/4 = 43$, where N is the number of water molecules in idealized unit cell of TS-I and Z is the number of guest molecules in the unit cell (since all water molecules are four-connected, $\Delta = 0$) and $b = 2h = 43 \times 2 = 86$; (2) inclusion of guest moieties causes a removal of chains of four framework vertices (Fig. 5a), resulting in the decreased hydrate number $h = 43 - 4 = 39$ and $b = 86 - 13 = 73$; (3) inclusion of oxygen atoms of carboxyl group in the γ and β positions of the host water framework (Fig. 5b) yields five additional O···O pairs suitable for hydrogen bonding, $b = 73 + 5 = 78$; the hydrate number and the number of donor hydrogen atoms being preserved. This framework is proton-balanced, $\Delta = 2h - b = 0$. Inclusion of "guest" water molecules causes the hydrate number to increase up to $h = 39.81(3)$. The Δ value depends on the accepted model of inclusion of the "guest" water molecules. The present model of inclusion of the "guest" water molecules within distorted pentagonal dodecahedra with three inward vertices leads to a proton deficient structure with $\Delta = -0.81(3)$, *i.e.* 0.990 protons per each hydrogen bond. According to the structure model proposed by Jeffrey and co-workers for the hydrate of tetrabutylammonium benzoate $(C_4H_9)_4NC_6H_5CO_2{\cdot}39.5H_2O$,[2] water molecules are arranged in distorted pentagonal dodecahedra with two inward vertices yielding the proton-balanced structure. The vacant D^1 cavities have on average 0.5 and 1.2 inward vertices each for the first and the second model, respectively. Most likely, an intermediate situation with the smaller proton deficiency and the larger number of little distorted cavities is actually realized. It is known, that in the water systems the cluster $(H_2O)_{21}H^+$ exhibits exceptional stability and there is evidence that it represents a pentagonal dodecahedra with encaged H_3O^+.[35] Additional experimental and theoretical studies are necessary to clarify this question.

The formation of a variety of hydrated solid phases with insignificant differences in compositions and melting points is an attribute of tetraalkylammonium salt–water systems.[3,25,26,31,36–38] Phase behavior of the tetraalkylammonium carboxylate–water systems is particularly rich,[26] but the number of polyhydrates in these systems remains controversial.[26,37] As evident from Table 1, the number of polyhydrates in a $(C_4H_9)_4NC_4H_9CO_2$–H_2O binary system reported by different authors varies from one[27] up to six,[25,26] but crystal structures remained unexplored. The detailed crystal structure of one of the six polyhydrates of tetrabutylammonium valerate studied in the present work is the first step to understanding crystal chemical peculiarities of hydration in this and similar systems. Unfortunately, we have not succeeded in growing the crystals of other polyhydrates in this system. The growth of metastable hydrated phases is a very difficult problem. Although some of them remain in metastable state for a long time, single crystals suitable for X-ray analysis have not been obtained so far.

Prior to the present work, the information about the structures of ionic clathrate hydrates of tetraalkylammonium carboxylates was limited to two structures only: tetragonal tetrabutylammonium benzoate $(C_4H_9)_4NC_6H_5CO_2{\cdot}39.5H_2O$[2] and orthorhombic tetraisopentylammonium propionate $(i\text{-}C_5H_{11})_4NC_2H_5CO_2{\cdot}36H_2O$.[3] The comparison of the above-mentioned structures and tetragonal $(C_4H_9)_4NC_4H_9CO_2{\cdot}39.8H_2O$ reported here reveals their common topological features: (1) the formation of five-compartment cavities

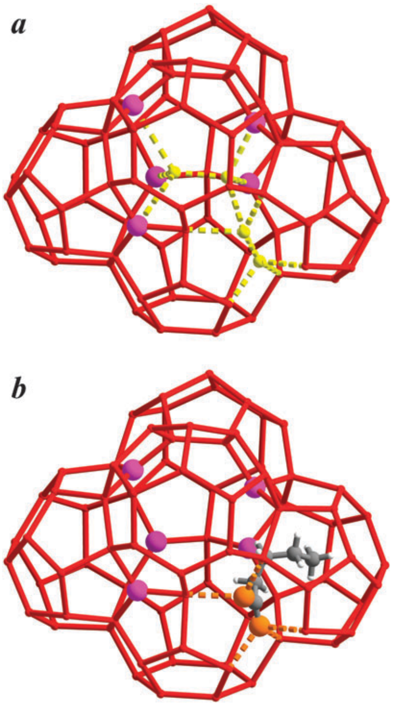

Fig. 5 The illustration of the hydrogen bonds balance calculation: (a) a removal of chain of four framework vertices; (b) inclusion of the valerate anion.

containing the alkyl chains of cations and anions, and (2) the inclusion of hydrophobic groups is accompanied by displacement of two "inner" water molecules of this combined cavity. This discriminates them from ionic clathrate hydrates of tetrabutyl- and tetraisopentylammonium halides for which the formation of four-compartment cavities and displacement of one "inner" water molecule are inherent.[1,31,32,37] Let us note that in earlier discussions of the experimental hydrate numbers of polyhydrates of tetrabutylammonium valerate derived from the phase diagram,[25,26,37] the authors assumed that inclusion of the cation is accompanied by the displacement of one water molecule from the idealized host framework. Notably, butyl chains of the cation are located in four-compartment cavities, and the butyl group of the anion occupies a separate cavity. Taking into account that the oxygens of the carboxyl group substitute two water molecules of the idealized host framework, the ideal hydrate number for the tetrabutylammonium valerate hydrate of TS-I must be 40, being in good agreement with the experimental value 39.7. In the present work we demonstrated that the ideal stoichiometry for tetrabutylammonium valerate hydrate of TS-I is $(C_4H_9)_4NC_4H_9CO_2{\cdot}39H_2O$ and additional 0.8 of water molecules come from enclathration of "guest" water molecules within distorted D-cavities.

Another general feature is that the inclusion of guest molecules breaks the site symmetry, however lowering of structure symmetry does not occur owing to spatial averaging of statistical disordered cavities.

It is necessary to emphasize that the obtained adequate model of disordering made it possible to find the detailed geometrical model of inclusion of guest moieties for the TS-I hydrates (for TS-I of $(C_4H_9)_4NC_6H_5CO_2{\cdot}39.5H_2O$ hydrate[2] studied previously, only a solution with an R-value as high as 17.5% was obtained). These results can be useful both for the refinement of characteristics of this structure by computer simulation techniques, and for assessing the validity of structural models of tetrabutylammonium carboxylate hydrates with a higher degree of disordering.

This structure solution revealed some uncertainties regarding different configurations of distorted D cages, which cannot be explicitly resolved with X-ray diffraction techniques. The present structure model can become a basis for clarifying these features by other methods.

Conclusion

The preparation and crystal structure of the tetragonal ionic clathrate hydrate of tetrabutylammonium valerate $(C_4H_9)_4NC_4H_9CO_2{\cdot}39.8H_2O$ are reported. Due to the high symmetry of host crystal lattices and inevitable disorder of the guest components the hydrate structures like this require extensive modeling as an integral part of the structure solution procedure. The ideal stoichiometry of the hydrate has been revealed and the details of the hydrate framework and inclusion mode of the guest salt have been obtained.

The analysis of the peculiarities of the structures of ionic clathrate hydrates of tetrabutyl- and tetraisoamylammonium carboxylates $(C_4H_9)_4N(C_4H_9CO_2){\cdot}39.8H_2O$ presented in this paper and previously studied structures $(C_4H_9)_4NC_6H_5CO_2{\cdot}39.5H_2O$,[2] $(i\text{-}C_5H_{11})_4NC_2H5CO_2{\cdot}36H_2O$[3] showed that in an estimation of the ideal stoichiometry of similar structures, not only does displacement of two water molecules from the idealized clathrate hydrate lattice by carboxy-anion have to be taken into account, but also replacement of two water molecules by the central nitrogen atom of guest salt molecule.

Acknowledgements

This work was performed in the frame of bilateral Scientific Cooperation Program between Nikolaev Institute of Inorganic Chemistry SB RAS and Institute of Physical Chemistry PAS. Financial support from Russian Foundation of Basic Research (Grant 09-03-00367) is gratefully acknowledged.

References

1 G. A. Jeffrey, in *Comprehensive Supramolecular Chemistry*, ed. D. D. MacNicol, F. Toda and R. Bishop, Pergamon, Oxford, 1996, ch. 23, vol. 6, pp. 757–788.
2 M. Bonamico, G. A. Jeffrey and R. K. McMullan, *J. Chem. Phys.*, 1962, **37**, 2219.
3 K. Suwinska, J. S. Lipkowski, Yu. A. Dyadin, V. Yu. Komarov, I. S. Terekhova, T. V. Rodionova and A. Yu. Manakov, *J. Inclusion Phenom. Macrocyclic Chem.*, 2006, **56**, 331.
4 E. D. Sloan Jr, *Nature*, 2003, **426**, 353.
5 A. K. Sum, C. A. Koh and E. D. Sloan, *Ind. Eng. Chem. Res.*, 2009, **48**, 7457.
6 E. D. Sloan and C. A. Koh, in *Clathrate Hydrates of Natural Gases*, Chemical Industries Series, 119, ed. H. Heinemann and J. G. Speight, 3rd edn, CRC Press, Boca-Raton, London, New York, 2008, pp. 1–721.
7 I. Tanasava and S. Takao, *Proceedings of the Fourth International Conference on Gas Hydrates*, Yokohama, 2002.

8 M. Darbouret, M. Cournil and J.-M. Herri, *Proceedings of the Fifth International Conference on Gas Hydrates*, Trondheim, Norway, 2005.

9 M. Darbouret, M. Cournil and J.-M. Herri, *Int. J. Refrig.*, 2005, **28**(5), 663.

10 H. Oyama, W. Shimada, T. Ebinuma, Y. Kamata, S. Takeya, T. Uchida, J. Nagao and H. Narita, *Fluid Phase Equilib.*, 2005, **234**, 131.

11 M. Arjmandi, A. Chapoy and B. Tohidi, *J. Chem. Eng. Data*, 2007, **52**, 2153.

12 S. Hashimoto, T. Sugahara, H. Sato and K. Ohgaki, *Chem. Eng. Sci.*, 2006, **61**, 7884.

13 S. Hashimoto, T. Sugahara, M. Moritoki, H. Sato and K. Ohgaki, *Chem. Eng. Sci.*, 2008, **63**, 1092.

14 A. Chapoy, R. Anderson and B. Tohidi, *J. Am. Chem. Soc.*, 2007, **129**, 746.

15 J. Sakamoto, S. Hashimoto, T. Tsuda, T. Sugahara, Y. Inoue and K. Ohgaki, *Chem. Eng. Sci.*, 2008, **63**, 5789.

16 B. Tohidi, J. Yang, A. Chapoy, R. Anderson and M. Arjmandi, Int. Patent., WO/2006/131738, 2006.

17 Y. Kamata, H. Oyama, W. Shimada, T. Ebinuma, S. Takeya, T. Uchida, J. Nagao and H. Narita, *Jpn. J. Appl. Phys.*, 2004, **43**, 362.

18 W. Shimada, T. Ebinuma, H. Oyama, Y. Kamata, S. Takeya, T. Uchida, J. Nagao and H. Narita, *Jpn. J. Appl. Phys.*, 2003, **42**, L129.

19 D. L. Li, J. W. Du, S. S. Fan, D. Q. Liang, X. S. Li and N. S. Huang, *J. Chem. Eng. Data*, 2007, **52**, 1916.

20 W. Lin, A. Delahaye and L. Fournaison, *Fluid Phase Equilib.*, 2008, **264**(1–2), 220.

21 F. Ahmadloo, G. Mali, A. Chapoy and B. Tohidi, *Proceedings of the 6th International Conference on Gas Hydrates*, Vancouver, Canada, 2008.

22 K. Shin, Y. Kim, T. A. Strobel, P. S. R. Prasad, T. Sugahara, H. Lee, E. D. Sloan, A. K. Sum and C. A. Koh, *J. Phys. Chem. A*, 2009, **113**, 6415.

23 I. Berger, V. Tereshko, H. Ikeda, V. E. Marquezz and M. Egli, *Nucleic Acids Res.*, 1998, **26**, 2473, N10, 2473–2480 Oxford University Press; Y.-K. Cheng and P. J. Rossky, *Nature*, 1998, **392**, 696; M. Nakasako, *J. Biol. Phys.*, 2002, **28**, 129; X. Chen, I. Weber and R. W. Harrison, *J. Phys. Chem. B*, 2008, **112**, 12073.

24 H. Tanaka, K. Nakanishi and K. Nishikawa, *J. Inclusion Phenom.*, 1984, **2**, 119; R. Schmid, *Monatshefte fur Chemie*, 2001, **132**, 1295.

25 Yu. A. Dyadin, L. A. Gaponenko and L. S. Aladko, *Izv. Sib. Otd. Acad. Nauk SSSR, Ser. Khim. Nauk*., 1986, **1**, 60.

26 Yu. A. Dyadin, L. A. Gaponenko, L. S. Aladko and S. V. Bogatyryova, *J. Inclusion Phenom.*, 1984, **2**, 259.

27 H. Nakayama and S. Torigata, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 171.

28 H. Nakayama and H. Usui, *J. Inclusion Phenom.*, 1984, **2**, 249.

29 H. Nakayama, T. Saiton and H. Uchida, *J. Inclusion Phenom. Mol. Recognit. Chem.*, 1990, **8**, 177.

30 G. Beurskens, G. A. Jeffrey and R. K. McMullan, *J. Chem. Phys.*, 1963, **39**, 3311.

31 J. Lipkowski, K. Suwinska, T. V. Rodionova, K. A. Udachin and Yu. A. Dyadin, *J. Inclusion Phenom. Mol. Recognit. Chem.*, 1994, **17**, 137.

32 V. Yu. Komarov, T. V. Rodionova, I. S. Terekhova and N. V. Kuratieva, *J. Inclusion Phenom. Macrocyclic Chem.*, 2007, **59**, 11.

33 Bruker AXS Inc. (2004): APEX2 (Version 1.08), SAINT (Version 7.03), SADABS (Version 2.11) and SHELXTL (Version 6.12). Bruker Advanced X-ray Solutions, Madison, Wisconsin, USA.

34 Z. Otwinowski and W. Minor, *Processing of X-Ray diffraction data collected in oscillation mode*, in *Methods in Enzymology. Macromolecular Crystallography. Part A*, ed. C. W. Carter and R. M. Sweet, Academic Press, New York, 1997, vol. 276, p. 307.

35 S. Wei, Z. Shi and A. W. Castleman, Jr., *J. Chem. Phys.*, 1991, **94**, 3268.

36 L. S. Aladko, Yu. A. Dyadin, T. V. Rodionova and I. S. Terekhova, *J. Struct. Chem.*, 2002, **43**, 990.

37 Yu. A. Dyadin and K. A. Udachin, *J. Struct. Chem.*, 1987, **28**, 394.

38 J. Lipkowski, V. Yu. Komarov, T. V. Rodionova, Yu. A. Dyadin and L. S. Aladko, *J. Supramol. Chem.*, 2002, **2**, 435.