

Clathrate Formation in the Water–Tetraisoamylammonium Propionate System: X-ray Structural Analysis of the Clathrate Hydrate $(i\text{-C}_5\text{H}_{11})_4\text{NC}_2\text{H}_5\text{CO}_2\cdot 36\text{H}_2\text{O}$

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Abstract

In this work X-ray single crystal structural analysis was carried out on the clathrate hydrate of tetraisoamylammonium propionate with the composition $(i\text{-C}_5\text{H}_{11})_4\text{NC}_2\text{H}_5\text{CO}_2\cdot 36\text{H}_2\text{O}$. The hydrate was found to have an orthorhombic structure in space group $Cmc2_1$ with unit cell parameters: $a = 21.281(2)$ Å, $b = 12.010(7)$ Å, $c = 24.768(3)$ Å (150 K). X-ray powder diffraction studies were performed of the hydrate phase, crystallized in the water– $(i\text{-C}_5\text{H}_{11})_4\text{NC}_2\text{H}_5\text{CO}_2$ system in the concentration range of the salt (10–25 wt%) that is the crystallization region of the studied polyhydrate, according to the phase equilibria data. It was found, that in the given concentration region the same hydrate of orthorhombic structure is formed, unit cell parameters, obtained at 20 °C: $a = 21.454(13)$ Å, $b = 12.156(4)$ Å, $c = 25.030(14)$ Å, are in a good agreement with the data of single crystal structural analysis.

Introduction

In the clathrate hydrates of tetraalkylammonium salts with simple anions (such as halides, sulfate, formate, etc.) water molecules together with the anions, form a crystalline host framework linked by hydrogen bonds (hydrophilic inclusion of the anion), while hydrocarbon chains of the cation fill the compartments of combined water polyhedra, formed by fusing four large cavities of the water framework, arranged in the structure tetrahedrally. The vertex shared by all four cavities is occupied by the central nitrogen atom of the cation, that displaces a water molecule and does not form any H-bonds with adjacent molecules (hydrophobic inclusion of the cation). The phase diagram and structural studies of water–tetraalkylammonium salts systems have revealed a number of polyhydrates, different in their structures, which can crystallize in these systems under specific conditions [1, 2].

In the clathrate hydrates of tetraalkylammonium salts with complex carboxylate anions hydrophilic–hydrophobic inclusion of the anion occurs: the carboxyl group is included in water framework in a

hydrophilic way through its oxygen atoms to form an edge of a polyhedron, whereas the hydrophobic part of the anion occupies the cavity of the water framework [3–5].

The comprehensive studies of water–tetraalkylammonium carboxylates systems showed, that the presence of a complex carboxylate anion in the guest molecule enhanced the variety of polyhydrate forms, crystallizing in the system [5, 6]. As distinguished from the clathrate hydrates of tetraalkylammonium salts with simple anions, in this case the clathrate hydrates with different compositions can form also within the same structural type, depending on the means of hydrophilic–hydrophobic inclusion of the carboxylate anion in the water framework [2, 5].

Proceeding with the investigations of clathrate hydrates of tetraalkylammonium carboxylates with respect to the ways of hydrophilic–hydrophobic inclusion of carboxylate anions in the water framework, in this work the single crystal X-ray structural analysis of the polyhydrate of tetraisoamylammonium propionate with the composition $(i\text{-C}_5\text{H}_{11})_4\text{NC}_2\text{H}_5\text{CO}_2\cdot 36\text{H}_2\text{O}$ was carried out. This is one of two stable hydrates, crystallizing in the water–tetraisoamylammonium propionate system, studied earlier by the DTA (differential thermal analysis) method (Figure 1), with m.p. +27.4 °C and the

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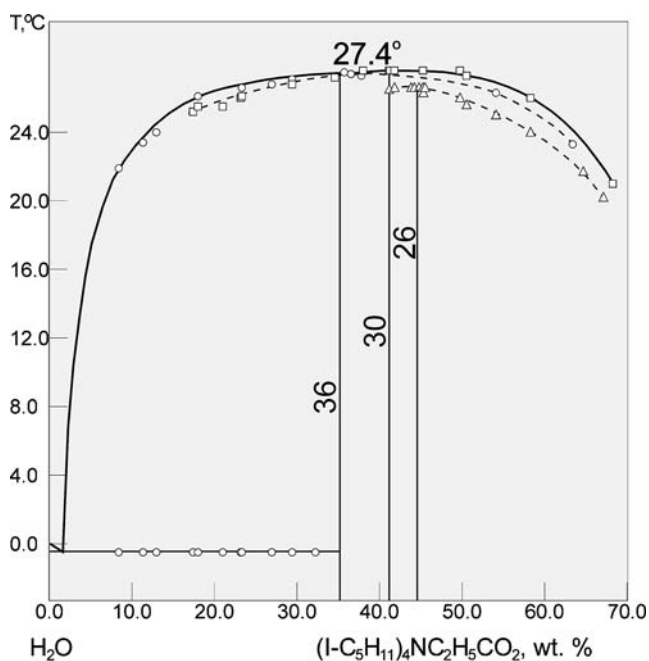


Figure 1. The phase diagram of the binary system H_2O –($i\text{-C}_5\text{H}_{11}$) $_4\text{NC}_2\text{H}_5\text{CO}_2$ in the region of clathrate formation.

hydration number, resulting from 5 preparative analyses, 36.48 ± 0.25 , $\rho(\text{exp}) = 1.041 \text{ Mg m}^{-3}$ [7]. In order to confirm the data of phase equilibria, in this work X-ray powder diffraction studies were also performed on the hydrate phase, crystallizing in the system within the concentration ranges of tetraisoamylammonium propionate (10–25 wt%) that is the crystallization region of the studied polyhydrate.

Experimental

Preparation of crystals for X-ray studies

Aqueous solutions of tetraisoamylammonium propionate were prepared by neutralization reaction of propionic acid and tetraisoamylammonium hydroxide, synthesized, in turn, by the reaction between silver oxide and slightly soluble tetraisoamylammonium iodide. The content of tetraisoamylammonium propionate in the solution was determined by potentiometric titration of the sample with sodium tetraphenylborate using cation selective electrode. The water content in the sample was determined using the K. Fisher method.

The monocrystals for X-ray experiments were deposited at 20 °C from the solution, having the concentration ~15 wt% of tetraisoamylammonium propionate and were shaped as rhombic plates.

For X-ray powder diffraction studies the crystals were isolated from the solutions with concentration of tetraisoamylammonium propionate varying in the ranges 10–25 wt%.

Structure determination

X-ray structural analysis of the polyhydrate ($i\text{-C}_5\text{H}_{11}$) $_4\text{NC}_2\text{H}_5\text{CO}_2 \cdot 36\text{H}_2\text{O}$ was carried out at 150(2) K on a Nonius Kappa CCD diffractometer (MoK α radiation, $\lambda = 0.71073 \text{ \AA}$, graphite monochromator). Data reduction and cell refinement were made using program packages Denzo and Scalepack [8] in the orthorhombic C-lattice (Table 1). The structure was solved by direct method and refined by full-matrix least squares on F^2 using SHELX-97 [9] package in the space group $Cmc2_1$. Thermal parameters of ordered oxygen atoms of water molecules and carbon atoms of the propionate-anion were refined anisotropically. Thermal parameters of other non-hydrogen atoms were refined isotropically. Positions of hydrogen atoms of alkyl chains were determined geometrically. Positions of hydrogen atoms of water molecules were not determined. Restraints (with $\sigma = 0.10$ and 0.20 for bond and angle distances) on interatomic distances in the tetraisoamylammonium cation were used to avoid residual shifts of its atoms.

X-ray powder diffraction studies were performed at 20 °C with Bruker D8 Advanced diffractometer (CuK α radiation), the geometry is Bragg-Brentano. The powder diffraction patterns were recorded in θ – 2θ scan mode with step 0.02 deg. in 2θ . The typical diffraction pattern of the hydrate phase ($i\text{-C}_5\text{H}_{11}$) $_4\text{NC}_2\text{H}_5\text{CO}_2 \cdot 36\text{H}_2\text{O}$ is shown in the Figure 2.

Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 266420.

Table 1. Crystal data and structure refinement for ($i\text{-C}_5\text{H}_{11}$) $_4\text{NC}_2\text{H}_5\text{CO}_2 \cdot 36\text{H}_2\text{O}$

| Chemical formula | $\text{C}_{23}\text{H}_{121}\text{NO}_{38}$ |
|---|---|
| Formula weight | 1020.21 |
| Temperature | 150(2) K |
| Crystal system, space group | orthorhombic, $Cmc2_1$ |
| Unit cell dimensions | |
| <i>a</i> | 21.281(7) Å |
| <i>b</i> | 12.010(2) Å |
| <i>c</i> | 24.768(3) Å |
| Volume | 6330(4) Å ³ |
| Z, calculated density | 4, 1.070 Mg m ⁻³ |
| Absorption coefficient | 0.101 mm ⁻¹ |
| <i>F</i> (0 0 0) | 2280 |
| Crystal size | 0.40 × 0.20 × 0.20 mm |
| θ range for data collection | 3.14–20.75° |
| Index ranges | |
| <i>h</i> _{min} , <i>h</i> _{max} | –21, 21 |
| <i>k</i> _{min} , <i>k</i> _{max} | –11, 11 |
| <i>l</i> _{min} , <i>l</i> _{max} | –24, 23 |
| Reflections collected/unique | 5862/3194 ($R_{\text{int}} = 0.0226$) |
| Data/restraints/parameters | 3192/47/282 |
| Goodness of fit on F^2 | 1.118 |
| <i>R</i> -values [$I > 2\sigma(I)$] | $R = 0.0578$, $wR = 0.1689$ |
| (for all data) | $R = 0.0600$, $wR = 0.1706$ |
| Largest diff. peak and hole | 0.29 and –0.22 e \cdot Å ⁻³ |

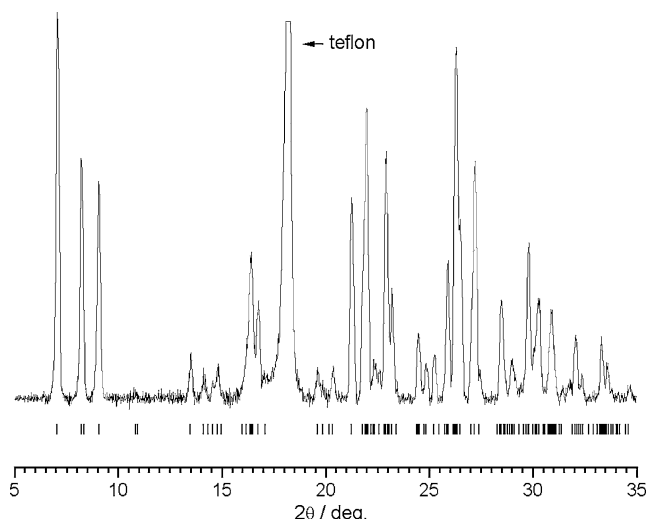


Figure 2. X-ray powder diffraction pattern of the sample of the clathrate hydrate $(i\text{-C}_5\text{H}_{11})_4\text{NC}_2\text{H}_5\text{CO}_2 \cdot 36\text{H}_2\text{O}$.

Results and discussion

As follows from the data of single crystal structural analysis (Table 1) the hydrate was found to have the orthorhombic structure, space group $Cmc2_1$ with unit cell parameters: $a = 21.281(2) \text{ \AA}$, $b = 12.010(7) \text{ \AA}$, $c = 24.768(3) \text{ \AA}$ (150 K).

X-ray powder diffraction data of the hydrate phase (Figure 2), crystallized in the water– $(i\text{-C}_5\text{H}_{11})_4\text{NC}_2\text{H}_5\text{CO}_2$ system in the concentration range of the salt 10–25 wt%, are in a good agreement with the data of single crystal structural analysis. It was found, that in all regions studied the same hydrate of orthorhombic structure is formed, unit cell parameters, obtained at 20 °C, are $a = 21.454(13) \text{ \AA}$, $b = 12.156(4) \text{ \AA}$, $c = 25.030(14) \text{ \AA}$.

The clathrate water framework of the polyhydrate studied is isostructural to that of tetraisoamylammonium fluoride polyhydrate with the composition $(i\text{-C}_5\text{H}_{11})_4\text{NF} \cdot 38\text{H}_2\text{O}$.¹ The idealized water framework corresponds to hypothetical hexagonal structure I (HS-I) of the gas hydrates, having $P6/mmm$ symmetry, and is composed of 12-hedral (D), 14-hedral (T) and 15-hedral (P) cavities. The elementary unit contains 4T, 4P and 6D cavities, giving the ideal stoichiometry $8\text{X} \cdot 6\text{Y} \cdot 80\text{H}_2\text{O}$ [1].

Inclusion of tetraisoamylammonium propionate results in reduction of the idealized water framework symmetry to $Cmc2_1$. In this case the structure contains 5 symmetrically independent types of cavities, the centres of those occupying the following positions: $\text{D}^1 - 8b$, $\text{D}^2 - 4a$, $\text{T}^1 - 4a$, $\text{T}^2 - 4a$, $\text{P} - 8b$. Two types of the face-sharing polyhedra layers, perpendicular to the $[0\ 0\ 1]$ direction, can be distinguished: the layers consisting of D^1 and D^2 -cavities (D-layer, Figure 3) and those consisting of P-cavities (P-layer, Figure 4). The packing of alternating D- and P-layers in the structure gives rise to the arrangement of polyhedra columns, composed of

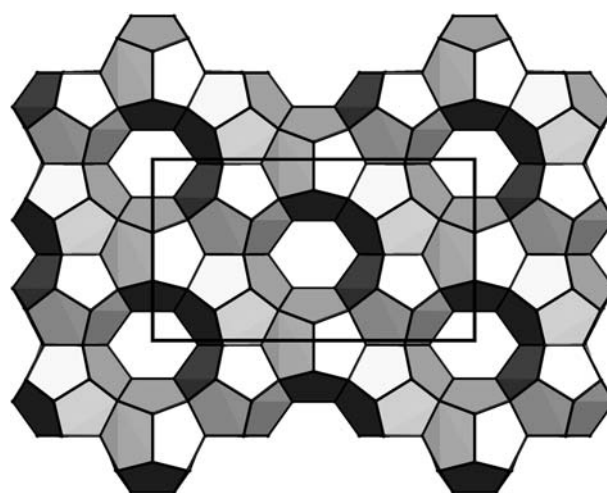


Figure 3. The tetraisoamylammonium propionate polyhydrate. The layer of face-sharing 12-hedral (D) polyhedra, perpendicular to the $[0\ 0\ 1]$ direction.

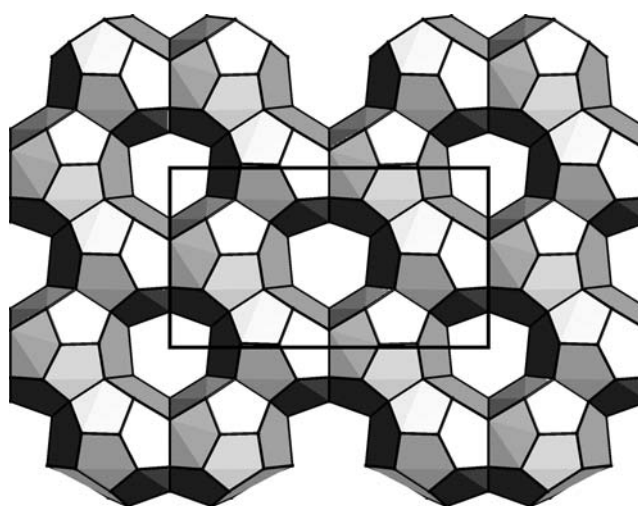


Figure 4. The tetraisoamylammonium propionate polyhydrate. The layer of face-sharing 15-hedral (P) polyhedra, perpendicular to the $[0\ 0\ 1]$ direction.

alternating T^1 and T^2 -cavities, sharing hexagonal faces (Figure 4).

The columns of D^1 -polyhedra, directed along $[0\ 1\ 0]$, remain unoccupied. The other types of polyhedra are involved in the formation of the combined five-sectioned cavities $\text{D}^2 \cdot \text{T}^1 \cdot \text{T}^2 \cdot 2\text{P}$, in which the cation–anion pairs of the guest molecules are located (Figure 5). Isoamyl chains of the cation are accommodated within four compartments of the combined cavity: T^1 , T^2 and two P-cavities, whereas the hydrophobic part of the propionate-anion is arranged in the D^2 -cavity (Figure 6).

It is necessary to note that this new type of the combined cavity was found in the structures of the clathrate hydrates for the first time.

Inclusion of the guest molecule causes the displacement of two 'inner' water molecules of the combined $\text{D}^2 \cdot \text{T}^1 \cdot \text{T}^2 \cdot 2\text{P}$ cavity (in the idealized water framework these molecules lie on the edge, common for two P-cavities and T-cavity), one of which is replaced by the central nitrogen atom of the cation. Two addi-

¹This structure was solved by Jeffrey [10] and is also orthorhombic, space group $Pbmm$ with a pseudo-hexagonal unit cell.

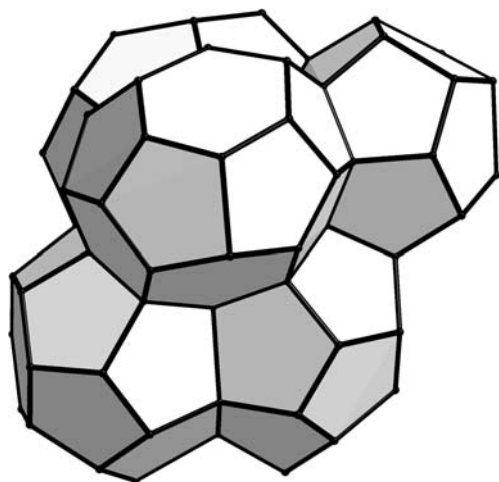


Figure 5. The combined five-sectioned cavity $D^2\cdot T^1\cdot T^2\cdot 2P$.

tional water molecules are replaced by two oxygen atoms of the carboxyl group, forming an edge of D^2 -section of the combined cavity. These rearrangements of the water framework lead to the hydrate stoichiometry: $(i-C_5H_{11})_4NC_2H_5CO_2\cdot 36H_2O$, the hydration number being consistent the analytical data: 36.48 ± 0.25 [7]. The tetraisoamylammonium cation and the propionate-anion are disordered over two positions in accordance with *mirror* symmetry (Figure 7). The lengths of hydrogen bonds in the water-anionic framework lie mainly in the range 2.74–2.84 Å. Shortened hydrogen bond distances are found around the oxygen atoms O01w and O02w that may be related to insufficient resolution of the electron density peaks of these oxygen

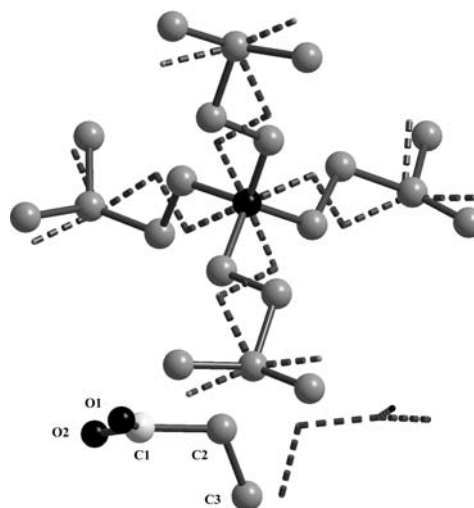


Figure 7. The tetraisoamylammonium propionate polyhydrate. Disorder of the alkyl groups of the cation and the propionate anion in accordance with mirror-symmetry is shown.

atoms and those of the carboxyl group (O1 and O2, Figure 7). This supposition is confirmed by the fact that O1–C1 and O2–C1 distances are significantly elongated (1.267(18) and 1.294(13) Å, respectively). Elongation of hydrogen bonds also takes place for the O16w (that belongs to T^1T^2 -sections of one combined cavity and two P-sections of another one) and O19w (that belongs to T^1T^2 -sections of one combined cavity and P-sections of two others). Hydrogen bond angles vary in the broad range (minimum value $92.7(2)^\circ$ for O13w...O11w...O18w angle, maximum value $140.0(2)^\circ$ for O19w...O16w...O19w' angle), that points, in our

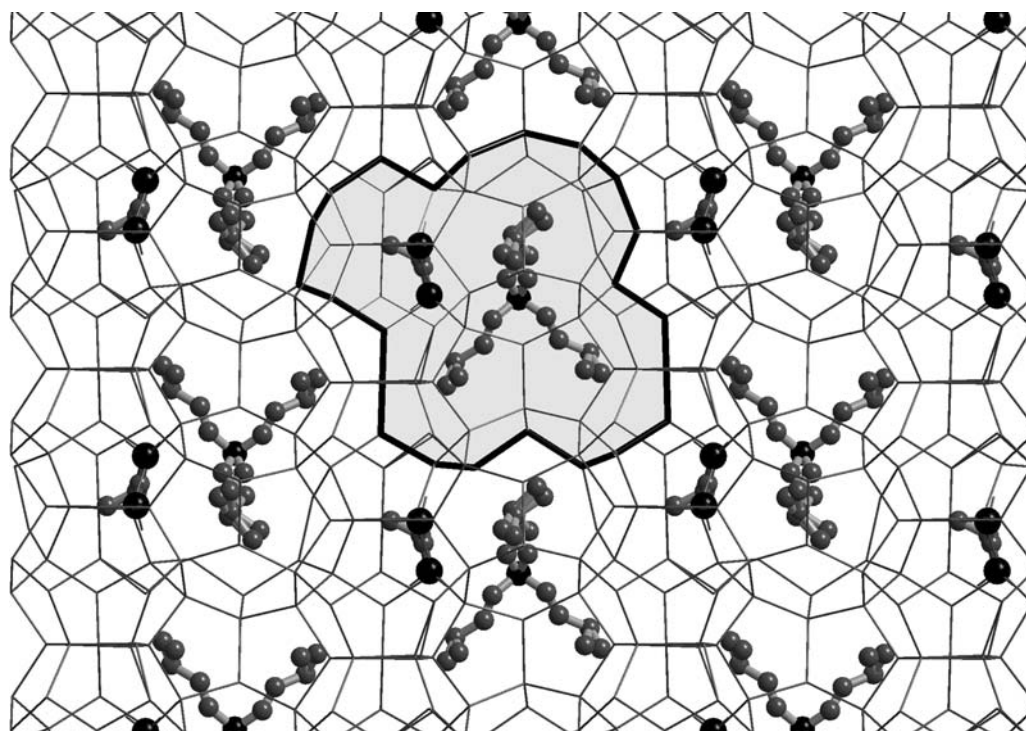


Figure 6. Accommodation of the tetraisoamylammonium cation and the propionate anion in the polyhydrate structure. The combined $D^2\cdot T^1\cdot T^2\cdot 2P$ cavity is marked.

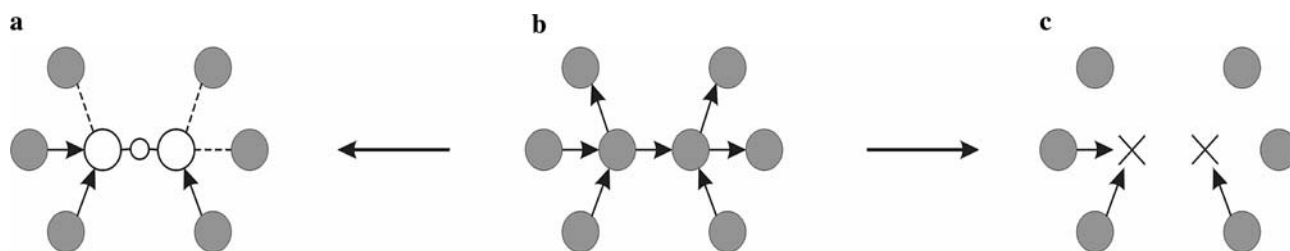


Figure 8. The scheme of hydrogen bonding in the water clathrate framework: ‚lack’ of hydrogen bonds (dotted lines) caused by replacement of two water molecules of the framework (gray circles) by two oxygen atoms (large white circles) of the carboxyl group (small white circle represents carbon atom of the carboxyl group) Hydrogen bonds in the water clathrate framework (marked by arrows) (c) ‚excess’ of hydrogen atoms caused by displacement of two water molecules from the framework.

opinion, to significant (however, not complete) proton ordering in this compound.

It is necessary to note that in this structure the number of short O...O distances (excluding oxygen atoms of the carboxyl group) is equal to the number of hydrogen atoms of the water molecules. This is possible due to the described rearrangement of the water framework: since the replacement of two hydrogen bonded water molecules in the tetrahedral water framework by two oxygen atoms of the carboxyl group results in the ‚lack’ of hydrogen atoms (Figure 8a) in comparison with the number of those required for the potential hydrogen bonds (short O...O distances, Figure 8b), the additional rearrangements, resulting in the appearance of ‚excess’ hydrogen atoms should be expected. In the studied structure the ‚lack’ of hydrogen atoms is compensated by the “excess” of those arising from the displacement of two additional water molecules in the framework (one of which is replaced by nitrogen atom of the cation), as described above (Figure 8c). Apparently, for other clathrate hydrates of tetraalkylammonium carboxylates, similar or more complex rearrangements of water frameworks may be assumed.

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