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Towards clathrates. 2. The frozen states of hydration of *tert*-butanol

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Abstract: A new crystal structure of *tert*-butanol and water crystallizing as the decahydrate is reported. The crystallization of the mixture in the desired molar ratio was performed in a capillary placed directly on a goniometer of a single crystal diffractometer at 200 K and ambient pressure using focused IR laser radiation. The crystals were grown while the melting zone formed by the IR laser was moved along the capillary. Usually the crystallization process should be long enough (hours) in order to obtain a good quality single crystal. However, in the case of *tert*-butanol decahydrate, such a long process led to separation of the ice and alcohol. Only fast crystallization taking tens of seconds allowed crystallization of the desired crystalline phase. In the decahydrate *tert*-butanol molecules are located in channels formed by water molecules. Hydroxyl groups are anchored to the water framework via hydrogen bonds. All water molecules in the structure have hydrogen atoms disordered equally over two sites; the hydroxyl group is likewise disordered. This effect is observed at both, 200 K and 100 K. Raman spectra recorded for the crystalline phase suggest dynamic disorder at higher temperature, converting to static at lower T . The decahydrate of *tert*-butanol, together with already known its *di*- and *hepta*-hydrates, display similar features to those observed for series of *tert*-butylamine hydrates. The latter structures behave as frozen steps of amine hydration observed as crystal structures leading, at maximum dilution, to hexagonal ice. Hydrates of *tert*-butanol nicely follow this tendency completing the relationship found for the *tert*-butylamine: water system.

Keywords: hydrates; hydrate clathrates; *in situ* crystallization; *tert*-butanol; water.

Dedicated to: Professor Roland Boese on the occasion of his birthday.

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Introduction

Some alcohols, predominantly methanol and ethylene glycol, are applied as hydrate formation inhibitors [1]. These compounds are used, e.g. in the oil industry to prevent blocking of the pipeline systems [2]. However, sometimes the formation of hydrate clathrates of alcohols, including methanol occurs, proven by liquid X-ray diffraction [3] or DSC experiments, combined with dielectric relaxation techniques [4]. Even solid-state clathrates of alcohols in the presence of CH_4 as a template occur, as shown by thermal ambient and elevated pressure experiments on *n*-propanol [5], by Raman spectroscopy and PXRD experiments on butanol isomers [6], and X-ray diffraction studies on *n*-propanol [7]. Still there are limited reports of binary structures containing alcohol and water, which might be associated with the tendency to vitrification of such liquids on cooling. In addition, pure low weight alcohols are generally considered as scarcely crystallizing compounds. Some of them, like ethylene glycol mixed with other ingredients, are ideal fluids for organ cryopreservation [8]. However, crystallization of these alcohols is still possible [9–12]. In the case of scarcely crystallizing compounds like methanol [13], *in situ* high pressure experiments are extremely helpful for investigating the influences of p and T on the investigated system [14–16]. Known binary alcohol-water single crystal structures, according to analyses based on the Cambridge Structural Database [17], usually contain a small number of H_2O molecules – these are mostly hemihydrates [18, 19]. Some exceptions are diols with pinacol as an example forming hexahydrate [20, 21]. However, in case of diols, one should have in mind that the number of water molecules assigned to each hydroxyl group is half of the total number.

Phase diagrams for *tert*-butanol water mixtures are known both for ambient [22, 23] and elevated pressures [24]. The aqueous solution of the alcohol were also studied in order to increase efficiency of freeze-drying processes for pharmaceutical industry [25–27].

For *tert*-butanol, two hydrates are known: *di*- and *hepta*-hydrates [28], the latter can be considered as a semi-clathrate [29]. This term was used to define ionic hydrates similar to clathrates; but with larger cages occupied by quaternary ammonium salts the meaning can be

extended to systems with 3-D water frameworks but with hydrophilic groups (NH₂, OH, etc.) incorporated into the water framework. To distinguish between mentioned above systems the use of “non ionic semi-clathrates” term in the latter case is proposed. The behavior of alcohols, which are rather reluctant to cocrystallize with water, is in contrast to amines which readily form hydrate systems with [30, 31] or without the presence of additional molecules [32–35]. With low water contents, structures of these binary amine hydrates are typical for cocrystals with usually ordered molecules and well-defined H-bonds. With more H₂O species, such molecules form non ionic semi-clathrates [36], or structures similar to hydrate clathrates [37]. However, unlike the hydrate clathrates of natural gas, all these amine hydrate structures display positional disorder of the water framework proving the presence of hydrogen bonds between guest NH₂ groups and host H₂O molecules. The organic compound forming the largest number of hydrates is *tert*-butylamine with seven crystal structures: 1/4, 1, 7/4, 7³/₄, 9³/₄, 11 and 17 hydrates, all at ambient pressure [38–43]. Recent research has shown that, under elevated pressure, *tert*-butylamine forms even more hydrates [44]. Such an easy hydrate-formation property of this amine might be associated with its bulky shape and some shielding of the NH₂ group by the *tert*-butyl residue. Moreover, the amine hydrates behave like frozen stages of solvation at given concentrations, as demonstrated by the characteristic molar volume plot typical for liquid mixtures [41, 42]. With a larger water amount (9³/₄, 11, 17 hydrates) it crystallizes to form similar networks as observed in hydrate clathrates. Smaller amounts of water are not able to encapsulate the amine fully, resulting in non ionic semi-clathrate formation (the case of 7¹/₄ hydrate). Similarly, the only analogous water-rich structure to *tert*-butanol is a heptahydrate forming a non ionic semi-clathrate which nevertheless has a different topology with respect to the corresponding amine system. The question arises whether *tert*-butanol, similarly to *tert*-butylamine, is able to form more hydrates, and which structure is preferentially formed: a non ionic semi-clathrate or a hydrate clathrate-like system. To answer this question, crystallization experiments of *tert*-butanol-water mixtures were performed for more diluted solutions.

Methods

Crystallization and single crystal X-ray diffraction

Liquid mixture containing *tert*-butanol and water in the molar ratio of 1:10 was sealed in a thin-wall glass capillary ($\varnothing=0.4$ mm) which

was mounted on the goniometer of a single crystal diffractometer – Bruker D8 Venture four-circle system equipped with a Photon100 CMOS detector. The capillary with its contents was kept at 200 K using a GN2-flow low temperature device. Crystals suitable for X-ray diffraction experiments were obtained using the *in situ*, melting-zone procedure with an IR laser beam focused on the capillary [45].

Diffraction data were collected at both 200 K and 100 K using TRIUMPH monochromated Mo radiation ($\lambda=0.71073$ Å). The obtained sample was oligocrystalline [46] and consisted of many differently oriented crystals belonging to the same phase. The analysis of the reciprocal lattice of the collected sample was performed with help of the RLATT plug-in of the Bruker software [47]. A diffraction image with reciprocal lattice reconstruction and reflections of differently oriented domains is presented in the Supplementary Materials. Because the lattices of the oligocrystalline sample were partially overlapped (but not twinned) the further data processing was based on the two most strongly diffracting domains and performed using the Bruker SAINT [48] and TWINABS [49] software. The crystal structure was solved using direct methods [50] and refined with help of the SHELX package [51]. The atomic scattering factors were taken from the International Tables [52]. At the initial stages, the structure refinements at both temperatures, were based on two components of unmerged reflection data with refined ratio of the “twin” fractions (HKLF 5 and BASF options). The final refinements were performed on the merged reflections (HKLF 4 option) after averaging out the data in the WinGX software package [53]. The crystal data and the final structure refinement parameters for *tert*-butanol decahydrate measured at 200 K and 100 K are displayed in Table 1. The anisotropic displacement parameters together with atom numbering scheme are presented in Figure 1. At both temperatures, hydrogen atoms of the hydroxyl groups and H₂O molecules are equally disordered over two positions. These H atoms were positioned on lines joining neighboring O atoms with O–H distances fixed at 0.9 Å and 1.0 Å for the water and alcohol molecules, respectively. The final data completeness for both measurements below 95% is lowered due to the φ -scan method used during the data collection. The crystals grown are partially oriented along the capillary which have been kept parallel to the LT device; this limits the number of reflections accessible for the data collection.

Single crystal structures of *tert*-butanol decahydrate were deposited in Cambridge Structural Database with the following numbers: 1544083 and 1544084 for the 100 K and 200 K measurements, respectively.

Raman spectroscopy

For the obtained oligocrystalline *tert*-butanol decahydrate, Raman spectra were acquired at both 200 K and 100 K. The spectrum was also recorded after melting the sample for the liquid mixture at 275 K. The spectra were collected directly on the goniometer of the single crystal diffractometer with an *in situ* confocal Raman probe connected to an InduRAM system using a 532 nm Nd laser to provide the excitation.

Results and discussion

A crystallization procedure for obtaining good quality single crystals should be performed under rather stable

Tab. 1: Crystal data and structure refinement for *tert*-butanol decahydrate crystal.

	<i>Tert</i> -Butanol decahydrate at 100 K	<i>Tert</i> -Butanol decahydrate at 200 K
Composition	C ₄ H ₁₀ O + 10 × H ₂ O	C ₄ H ₁₀ O + 10 × H ₂ O
<i>M</i>	254.28	254.28
<i>T</i> /K	100(2)	200(2)
λ /Å	0.71073	0.71073
Size/mm	0.3 × 0.3 × 0.6	0.3 × 0.3 × 0.6
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
Unit cell parameters/Å, °	<i>a</i> = 9.0768(8) <i>b</i> = 9.0411(6) <i>c</i> = 19.9718(19) β = 92.087(3)	<i>a</i> = 9.1333(8) <i>b</i> = 9.0481(6) <i>c</i> = 20.1246(17) β = 92.176(2)
<i>V</i> [Å ³]	1637.9(2)	1661.9(2)
<i>Z</i> , <i>D_s</i> /g · cm ⁻³	4, 1.031	4, 1.016
μ [mm ⁻¹]	0.103	0.102
<i>F</i> (000)	568	568
θ_{\min} , θ_{\max}	2.98°, 25.05°	2.96°, 25.05°
Reflections collected/independent	24774/2733 [<i>R</i> _{int} = 0.1126 for 2 θ_{\max} = 50.74] ^a	26021/2831 [<i>R</i> _{int} = 0.1173 for 2 θ_{\max} = 50.77] ^a
Completeness	94.4% ^b	94.6% ^b
<i>T</i> _{max} , <i>T</i> _{min}	0.96, 0.74	0.96, 0.74
Reflections/constraints/parameters	2733/0/139	2781/0/140
Goof on <i>F</i> ²	1.104	1.061
<i>R</i> [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.0809 <i>wR</i> 2 = 0.2363	<i>R</i> 1 = 0.0869 <i>wR</i> 2 = 0.2570
<i>R</i> (all data)	<i>R</i> 1 = 0.0948 <i>wR</i> 2 = 0.2481	<i>R</i> 1 = 0.1099 <i>wR</i> 2 = 0.2883
ρ_{\max} , ρ_{\min} /e · Å ⁻³	0.535, -0.433	0.480, -0.398

^aData processing for multi-component crystal, HKLF5 refinement, conversion to HKLF4 format, final refinement.

^bData completeness lowered due to angular limits of goniometer movement for sample crystallized in capillary.

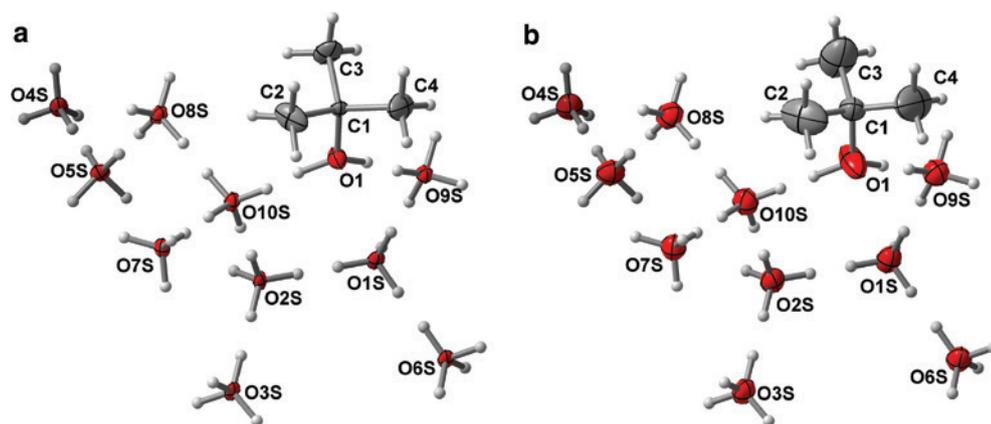


Fig. 1: Numbering scheme and thermal ellipsoid plot at 50% probability level for the asymmetric part of the unit cell of *tert*-butanol decahydrate measured at 100 K (a) and 200 K (b).

conditions. Consequently, in the case of using the IR laser induced melting zone approach, [37+6] the movement of the laser beam should be rather slow – perhaps some hours per cm. Otherwise the crystallization will result in too small or defective, twinned or randomly oriented

crystals. There are some exceptions of course – it is very easy to crystallize ice in a short time using the mentioned method. However, a slow movement of the IR laser generating the melting zone and applied to the overlaid mixture of *tert*-butanol and water (molar ratio 1:10) results in the

formation of hexagonal ice I_h only. Fast scanning, however, resulted in crystallization of the *tert*-butanol decahydrate. Unfortunately, the quality of the obtained crystals was poor – see the diffraction patterns and reciprocal lattice reconstructions shown in the Supplementary Materials. Nevertheless, the final crystal structure and refinement parameters are fully acceptable. The hydrate crystals were grown with a laser beam movement of approximately 5 mm/min. With a slower crystallization process, both components of the mixture were separated and crystallized in their pure phases. Only the fast laser scan resulted in the formation of thermodynamically not-stable crystals, quickly frozen at 200 K – the setting of the gas flow of the LT device. After the X-ray data collection the temperature was increased and, at 258 K, the crystals turned into a fine powder without melting. After increasing the temperature to 270 K, the powder diffraction rings gradually vanished and some separated diffraction spots appeared. This indicates that the obtained *tert*-butanol decahydrate crystals were sub-cooled with trapped molecules in the crystal lattice, and when warming to a transition temperature, the system relaxed to more stable phases – either ice and *tert*-butanol or to the thermodynamically stable *di*- and *hepta*-hydrates [28].

The resulting structure at 200 K has a ratio of one *tert*-butanol molecule and 10 water species in the asymmetric unit of the cell. No phase transition was detected between 200 K and 100 K, where a significant lowering of the thermal motions of the atoms can be observed – see Figure 1. Whereas the positions of the O atoms are precisely defined, each H atom of the H_2O molecule is equally disordered over two sites, exactly like in the structures of H-disordered polymorphs of ice and it is for the majority of hydrate clathrates. Observed hydrogen atom disorder of all water molecules implies disorder of the H atom of the hydroxyl group. In the crystal lattice, H_2O species form a 3-D network with intermolecular O...O distances ranging from 2.73 Å to 2.80 Å, and from 2.74 Å to 2.82 Å at 100 K and 200 K, respectively. Alcohol molecules are located in cavities with the hydroxyl groups engaged in strong hydrogen bonds – $O_{\text{hydroxyl}} \cdots O_{\text{water}}$ distances at 2.72 Å, 2.76 Å and 2.77 Å, 2.79 Å for the 100 K and 200 K structures, respectively. The hydrophobic part of the alcohol is surrounded by water molecules forming gaps. The closest environment of the *tert*-butyl alcohol is presented in Figure 2. In the structures small, empty cages formed by H_2O molecules are present. However, these cages are concave – some of their faces are irregular and distorted polygons. When the O8 and O9 atoms are linked, without taking into account bridging O8' atom (see Figure 2), the resulting cage can be considered to be the 4^35^6 type,

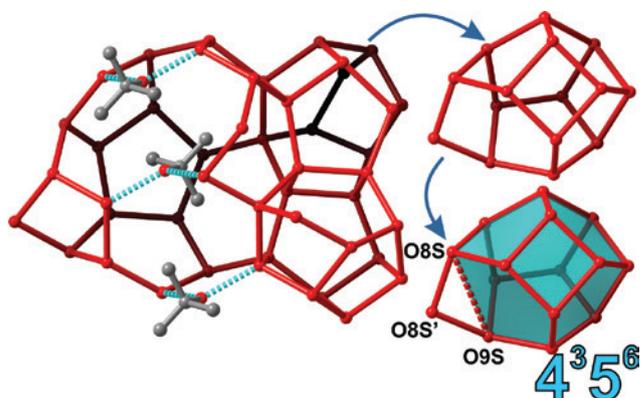


Fig. 2: Fragment of the water framework of the *tert*-butanol decahydrate showing distorted cage of a 4^35^6 type colored in cyan.

i.e. constructed from three squares and six pentagons. However, in the obtained cage the distance between the O8 and O9 atoms is far too large, yielding approx. 4.2 Å (at 100 K). This type of cage is too small to host any organic molecules, and can be also found, but in not distorted form, in $7^3/4$ and 11 hydrates of *tert*-butylamine [41, 42]. The cavities present around hydrophobic part of the alcohol molecules are arranged forming channels parallel to the [010] direction. This is shown in Figure 3a. The boundaries of these channels consist of water molecules forming irregular pentagons and hexagons, some of them distorted and bent – see Figure 3b–d. In some of these distorted polygons, smaller structures like quadrilaterals or even triangles can be found but with rather long contacts (≥ 3.9 Å) between selected O atoms located at the vertices. The distortion of polyhedra in the obtained structure is probably caused by the rather fast crystallization process and growing of a thermodynamically not-stable phase. In the previously mentioned $7^3/4$ hydrate of *tert*-butylamine, the structures of the 4^35^6 cages are not distorted, whereas the 11 hydrate of this amine exhibits some disorder in the water framework. This can be observed by alternative O sites with occupancies $< 10\%$, but it is due to the nature of the amine behaving as guest and being simultaneously engaged in hydrogen bonds with the host H_2O network. The channels formed in the structure of *tert*-butanol decahydrate are similar to those observed in the hexahydrate of pyrrolidine [36]. In the latter case, however, there are no additional small and empty cages. The secondary amine, similar to *tert*-butanol, is anchored via functional groups in the 3-D water framework. Contrary to the structure with alcohol in the amine hydrate, H_2O species form mostly non-distorted quadrilaterals and hexagons. The density of packing of the organic molecules in the channel (number of the molecules per 1 Å segment

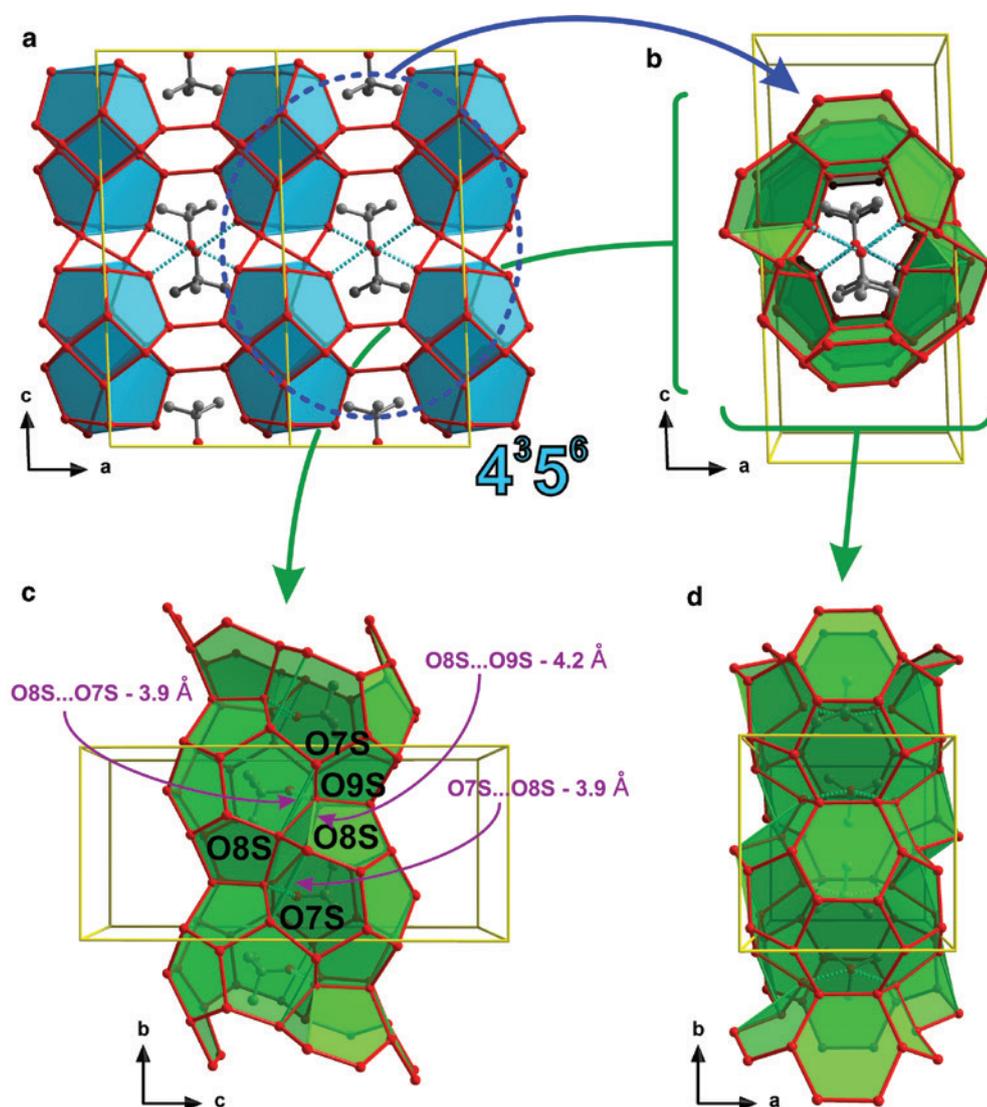


Fig. 3: Packing diagram of the *tert*-butanol decahydrate (a) showing 2D channels filled by the alcohol molecules viewed along [010] (b), [100] (c) and [001] (d) directions.

of the channel) is equal to 0.247 \AA^{-1} and 0.221 \AA^{-1} in the amine and alcohol hydrates, respectively. Thus, the pyrrolidine molecules are better packed in the channels than *tert*-butanol which is associated with the slightly bigger size of the latter molecule. Another example of a structure with similar channels and some small unoccupied voids is the $7\frac{3}{4}$ hydrate of *tert*-butylamine [41, 42]. In this case, the linear density of packing of the molecules per 1 \AA segment of the channel is equal to 0.232 \AA^{-1} . Thus, the amine molecules in the $7\frac{3}{4}$ hydrate are better packed in channels than the *tert*-butanol species in its decahydrate.

As mentioned earlier, *tert*-butylamine, the analogous molecule to *tert*-butanol, can form seven different hydrates at ambient pressure. When the density of these crystals is plotted against the number of water molecule per the

amine, a modified Morse function can be fitted [54]. It is also possible to generate an excess molar volume plot [41, 42] for the structures in a similar way as for liquid binary mixtures. Surprisingly, the data points representing the *tert*-butanol crystal structure and its hydrates are in very good agreement with trends observed in *tert*-butylamine. The dependence of the crystal density on the number of water species per organic molecule, together with excess molar volume plot is presented in Figure 4. The new *tert*-butanol decahydrate structure is denoted by a yellow star. On the upper diagram there are three different points representing neat *tert*-butanol. The most deviating point with the highest density is the *tert*-butanol polymorph crystallizing in the $P\bar{3}$ space group with the molecules forming isolated hexamers [55]. In the other polymorphs

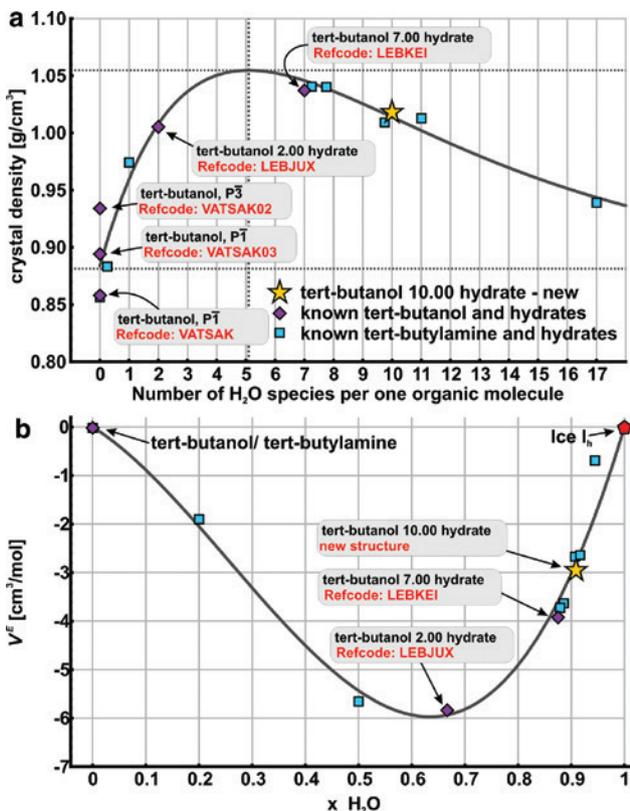


Fig. 4: Dependence of the crystal density based on the water contents for all known ambient pressure hydrates of *tert*-butylamine and *tert*-butanol (including neat compounds) (a), excess molar volume plot for all known ambient pressure hydrates of *tert*-butylamine and *tert*-butanol (b).

of *tert*-butanol and the neat *tert*-butylamine structure, the molecules interact via hydrogen bonds forming columns leading to less dense crystals [56, 57]. All the data points were scaled to a temperature of 173 K based on the thermal expansion of hexagonal ice [58, 59]. In the upper diagram the modified Morse function with formula

$$f(x) = s - d_e \cdot (1 - e^{-(a(x-r_e))})^2$$

was fitted to the data where $s=1.055(13)$, $d_e=0.173(66)$, $a=0.135(33)$ and $r_e=5.09(69)$. With the increase of the number of water molecules – x the function asymptotically approaches $s-d_e$, which is equal to $0.882 \text{ g} \cdot \text{cm}^{-3}$ – the expected density of structure containing only water molecules at 173 K. This value is close to the density of the actual hexagonal ice polymorph at 173 K, which is $0.929 \text{ g} \cdot \text{cm}^{-3}$. The given function fits all the data points very well, except perhaps for the discussed trigonal polymorph of *tert*-butanol. A similar behavior of the amine and alcohol hydrates can be deduced from the plots in spite of the different crystal architectures of the

presented compounds. Both the *hepta*- and *deca*-hydrates of *tert*-butanol are examples of non ionic semi-clathrates whereas hydrates containing *tert*-butylamine with similar numbers of water molecules are mostly clathrates with disordered water frameworks. This disorder comes from the amine-H₂O interaction. The lower diagram in Figure 4 represents an excess molar volume plot for crystalline hydrates of *tert*-butylamine and *tert*-butanol, depending on their molar fractions. Again, the point representing *tert*-butanol decahydrate is marked with a yellow star, as well as the data points representing *tert*-butanol hydrates, keeping the trend for the structures containing the amine. The fitted function is a Redlich–Kister polynomial [60] of the following form:

$$f(x) = x \cdot (1-x) \cdot (A_0 + A_1 \cdot (1-2 \cdot x))$$

where x is the molar fraction of water, $A_0=-21.755$, $A_1=15.053$ and $\sigma=0.410$.

This function is widely used for analyses of binary liquids. The behavior of the crystalline *tert*-butanol and *tert*-butylamine hydrates resembles liquid mixtures with each data point representing different frozen hydration steps. The observed negative molar volume of the given system is due to stronger interactions between *tert*-butanol/*tert*-butylamine and water molecules and due to more efficient packing of the species in the mixture than in pure phases. This is of course due to the formation of the hydrates; otherwise, the crystallization of ice and amine/alcohol instead of a multicomponent crystal would be energetically more favorable.

The analyses of the Raman spectra of the solid *tert*-butanol decahydrate and liquid mixture obtained after melting of the crystal displayed in Figure 5, shows that there are hydrogen bonds present between water and

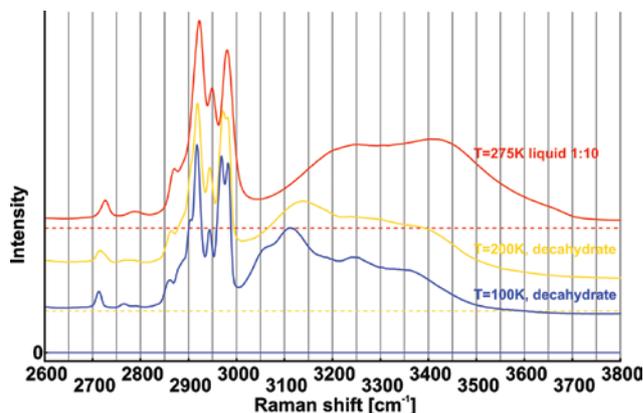


Fig. 5: Raman spectra of solid *tert*-butanol decahydrate compared with the spectrum of the melt.

hydroxyl groups. At lower temperatures, e.g. at 100 K, hydrogen bonds in *tert*-butanol decahydrate are even stronger than at 200 K. In the solid phase the complex band, corresponding to stretching of O–H bonds, is in the range 3000–3500 cm⁻¹. However, at both temperatures the positions of the H₂O hydrogen atoms are disordered over two alternative sites; the signals at 100 K are more intense and closer than at 200 K. This suggests that hydrogen atom disorder has a dynamic nature at higher temperatures while changing to static disorder on cooling. The Raman spectra of the liquid alcohol-H₂O mixture in the range 3000–3800 cm⁻¹ is very similar to the spectrum of pure water there is no evidence of hydroxyl group O–H stretching modes. This band should be located around 3365 cm⁻¹ as observed in liquid *tert*-butanol [61]. The lack of this band in the spectrum of the liquid mixture in Figure 5 is due to the small concentration of the alcohol and very weak intensity corresponding to hydroxyl O–H vibrations in general. Spectra with similar effects can be obtained for different solutions of *tert*-butanol in water [62]. However, there is one example of a *tert*-butanol mixed clathrate hydrate with methane, but there is no evidence of hydrogen bond formation between the alcohol and water [6]. In such a case, the O–H stretching mode is expected around 3600 cm⁻¹. Lack of this sharp band from the decahydrate of *tert*-butanol presented here, suggests that all organic molecules are hydrogen-bonded with water species, which can be directly taken from the single crystal data.

Conclusions

Two hydrates of *tert*-butanol are known: a *di*- and a *hepta*-hydrate. The low number is surprising when compared to the analogous *tert*-butylamine, for which seven different hydrates under ambient pressure are known. However, the two hydrates of *tert*-butanol can be considered as surprising in respect of the rather large number of alcohols known to co-crystallize reluctantly with water. Here, we report a new *tert*-butanol decahydrate crystal structure. The crystals were grown in a capillary containing water and alcohol in the desired molar ratio using focused IR laser radiation. The crystallization process was very short taking only tens of seconds instead of hours as in typical cases. In addition, the crystals turned to powder on heating before reaching the melting point. This suggests that the obtained decahydrate is a thermodynamically not-stable form, in contrast to the other *tert*-butanol hydrates. In the crystal lattice, water molecules interact via hydrogen bonds and form a 3-D network with channels

occupied by the alcohol molecules. The O...O distances in this structure are typical for ice and clathrate hydrates crystals yielding ca. 2.7 Å–2.8 Å.

Hydroxyl groups forming hydrogen bonds with H₂O molecules anchor the alcohol into the water framework. Thus, this structure can be considered to be a non ionic semi-clathrate. Moreover, there are small and empty cavities in the water framework which are characterized as unusual distorted 4³5⁶ polyhedra. In contrast, such polyhedra in 7³/₄ and 11 hydrates of *tert*-butylamine are not distorted. The distortion is probably due to the fast growth of this thermodynamically not-stable *tert*-butanol hydrate. In the crystal lattice of the decahydrate, hydrogen atoms of the hydroxyl group and all water molecules are equally disordered over two sites. This disorder is observed at both 200 K and 100 K. The Raman spectra also indicate the change of the disorder from dynamic to static on cooling. All together, hydrates of *tert*-butylamine and *tert*-butanol behave as frozen steps of hydration observed as crystal structures leading, at maximum dilution, to hexagonal ice. Hydrates of *tert*-butanol nicely follow the tendency observed for *tert*-butylamine [41, 42] completing the relationship found.

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