

# Phase and X-Ray Study of Clathrate Formation in the Tetraisoamylammonium Fluoride-Water System

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**Abstract.** The phase diagram of the binary (*i*-C<sub>5</sub>H<sub>11</sub>)<sub>4</sub>NF-water system has been studied in the clathrate formation region. Three polyhydrates have been discovered, two of which (1 : 38.9 and 1 : 32.7) are the known orthorhombic and tetragonal phases: *Pbmn*, *a* = 11.88, *b* = 21.53, *c* = 12.70 Å,  $\rho_{\text{meas}} = 1.019 \text{ g cm}^{-3}$  (0 °C), m.p. = 32.4 °C and *P4<sub>2</sub>/m*, *a* = 23.729, *c* = 12.466 Å,  $\rho_{\text{meas}} = 1.062 \text{ g cm}^{-3}$ , (0 °C), m.p. = 31.2 °C, respectively. A single crystal X-ray analysis of the novel clathrate hydrate (*i*-C<sub>5</sub>H<sub>11</sub>)<sub>4</sub>NF · 27 H<sub>2</sub>O is reported. This new clathrate hydrate is tetragonal, *I4<sub>1</sub>/a*, with *a* = 16.894(5), *c* = 17.111(2) Å, *Z* = 4, (–50 °C), and m.p. = 34.6 °C. Each (*i*-C<sub>5</sub>H<sub>11</sub>)<sub>4</sub>N<sup>+</sup> cation occupies a four-chamber cavity built of 15-hedra 7<sup>1</sup>6<sup>3</sup>5<sup>9</sup>4<sup>2</sup> (idealized description), with small vacant 5<sup>4</sup>4<sup>4</sup> cavities filling the intervening space.

**Supplementary Data** relevant to this paper have been deposited with the British Library as Supplementary Publication SUP 82162 (13 pages).

**Key words:** Clathrate hydrate, phase diagram, crystal structure, tetraisoamylammonium fluoride.

## 1. Introduction

Almost all studies on the formation of hydrates in the tetraisoamylammonium salt-water systems reported so far [1–6] suggest that this hydrophobic cation forms only hydrates with 38 water molecules per formula unit of the salt (except for tetraisoamylammonium polyacrylate [7] which has 42 water molecules). Jeffrey *et al.* [2, 3] have studied a 1 : 38 tetraisoamylammonium fluoride hydrate of orthorhombic symmetry in which the cation is accommodated in a four-chamber cavity T<sup>2</sup>P<sup>2</sup> (T = tetrakaidecahedron, P = pentakaidecahedron), and the dodecahedral D-cavities are vacant. Tetraisoamylammonium chloride, tungstate and chromate polyhedral hydrates studied simultaneously by the same authors [2] are isostructural with (*i*-C<sub>5</sub>H<sub>11</sub>)<sub>4</sub>NF · 38 H<sub>2</sub>O. The water-tetraisoamylammonium halide (fluoride, chloride, bromide, iodide) phase diagrams reported previously [1, 4–6,

8] have confirmed the presence of polyhydrates with 38 water molecules per cation in each of the systems.

Mindful of the fact that water and halide ions tend to form a variety of anionic frameworks with similar energies and that T and P cavities well stabilized by tetraisoamylammonium cations exist not only in clathrate hydrates with the stoichiometry 1 : 38 (peralkylonium cation : water), but also in the majority of other frameworks [9], we have undertaken a thorough examination of the  $(i\text{-C}_5\text{H}_{11})_4\text{NF}$ -water phase diagram, obtained solid phases and studied their properties [10]. We have indeed shown that two hydrates (1 : 38 and 1 : 27) having stable crystallization ranges, form in the system. The 1 : 32 hydrate of the well-known tetragonal structure I [9] is metastable with respect to the two others in the whole crystallization range.

## 2. Experimental

Tetraisoamylammonium bromide was prepared from isoamyl bromide and triisoamylamine by the Menshutkin reaction. An equimolar mixture of triisoamylamine and isoamyl bromide in acetonitrile was heated for 28 h. The crystals were crystallized from methylethylketone and dried at 50–60 °C under a pressure of 3–5 mm Hg.

An aqueous solution of tetraisoamylammonium fluoride was obtained from the metathesis of tetraisoamylammonium bromide and silver fluoride in water with precipitation of silver bromide. Polyhydrate crystals were obtained by concentration of the aqueous solution over phosphorus pentoxide in a vacuum drier. It should be noted that attempts to obtain solutions with concentrations higher than 60% wt. failed, as further concentration caused partial decomposition of the cation. The concentration of the salt was determined by potentiometric titration of tetraphenylborate with an ion-selective electrode [11], and that of water by the Fischer technique [12]. The total water and salt content was  $99.7 \pm 0.2\%$  wt. The density of the crystals was determined by the flotation method in a mixture of carbon tetrachloride and benzene at 0 °C.

Melting points and solid phase transformations were recorded by the DTA method. A chromel-copel thermocouple was calibrated with the help of a standard mercury thermometer. The reproducibility of the temperature measurement was  $\pm 0.02$  °C and the precision of measuring the phase transition temperature was  $\pm 0.2$  °C. The volume of the solution studied was 10  $\mu\text{L}$ . The solubility technique was used in several cases to specify the liquidus curve. The temperature stability was  $\pm 0.05^\circ$ . The crystals for the present X-ray study were obtained from an aqueous solution of approximately 23% wt.  $(i\text{-C}_5\text{H}_{11})_4\text{NF}$  at 25–28 °C. The X-ray study was performed by using crystals enclosed in glass capillaries. The structure was solved by direct methods (SHELX86 [13]) and refined by using SHELX76 [14]. A summary of the experimental X-ray data is given in Table I.

TABLE I. Data collection and structure analysis parameters.

Molecular formula	$(i\text{-C}_5\text{H}_{11})_4\text{NF} \cdot 27 \text{H}_2\text{O}$
Molecular weight	803.98
Unit cell parameter	$a = 16.894(5) \text{ \AA}$ $c = 17.111(2) \text{ \AA}$ $V = 4883.6 \text{ \AA}^3$ $Z = 4$
Calc. density [ $\text{g cm}^{-3}$ ]	1.094
Space group	$I4_1/a$
Diffractometer	CAD4 Enraf-Nonius
Radiation	graphite monochromatized Cu $K_{\alpha}$ , $\lambda = 1.5418 \text{ \AA}$
$2\vartheta_{\text{max}}$	$78^\circ$
Temperature	223 K
Absorption coefficient	$\mu = 8.18 \text{ cm}^{-1}$
Crystal size [mm]	$0.4 \times 0.4 \times 0.5$
Number of reflections	
measured	2656
unique	2561
used in the structure analysis	1978
Number of variables in refinement	178
Absorption and/or extinction correction	none
Final $R$ and $wR$ values	0.043, 0.048
Weighting scheme	unit weights
Residual extrema in final difference map [ $\text{e \AA}^{-3}$ ]	-0.14 to +0.16

### 3. Results

#### 3.1. PHASE DIAGRAM

The phase diagram of the binary tetraisoamylammonium fluoride-water system in Figure 1 indicates the existence of at least three polyhydrates of the following stoichiometries: 1 : 38.9; 1 : 32.7; 1 : 26.8; ( $h_{38}$ ,  $h_{32}$ ,  $h_{27}$ , respectively). Single crystals of the three compounds have been grown and some of their physical characteristics have been measured (densities, compositions, melting points, unit cell parameters given in Table II). Incongruent melting of the polyhydrate  $h_{38}$  occurs at  $32.0^\circ\text{C}$ , and congruent melting of this compound at  $32.4^\circ\text{C}$  occurs within the crystallization range of the hydrate  $h_{27}$ . The metastable part of the phase diagram characterizing the hydrate  $h_{38}$  was observed repeatedly which was presumably due to kinetic difficulties in the formation of the hydrate  $h_{27}$  which was stable under these conditions (see below).

The observation of the stable part of the phase diagram characterizing the  $h_{27}$  hydrate was possible only when freezing and melting the mixture of the correspond-

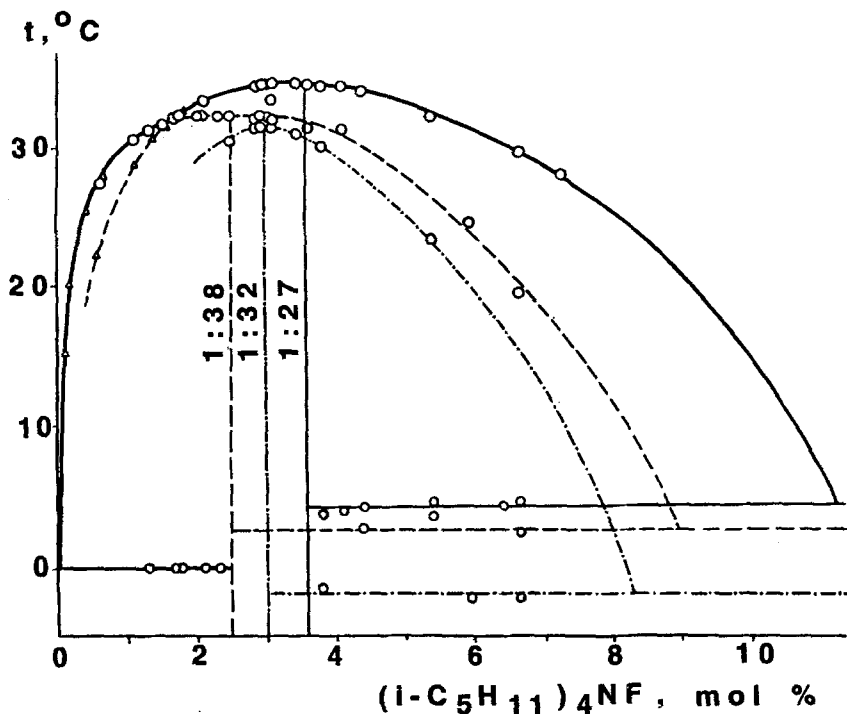


Fig. 1. Phase diagram of the  $(i\text{-C}_5\text{H}_{11})_4\text{NF}$ -water system in the clathrate formation region.

TABLE II. Some physical and crystallographic data of the tetraisoamylammonium fluoride hydrates.

Hydration number		Density [g cm <sup>-3</sup> ]		M.p. [°C]	Space group	Cell parameters [Å]			Z
expt.	struct.	expt. <sup>1</sup>	struct.			a	b	c	
38.9	—	1.019	—	32.4		11.88	21.53	12.70	2
—	38.0	1.022	0.990	31.2	<i>Pbmm</i>	12.08	21.61	12.822	2[2]
32.7	—	1.062	1.066 <sup>3</sup>	31.4	<i>P4<sub>2</sub>/m</i>	23.729		12.466 <sup>2</sup>	5
26.8	27.0	1.079	1.093	34.6	<i>I4<sub>1</sub>/a</i>	16.894		17.111 <sup>2</sup>	4
			1.085			16.937		17.161 <sup>1</sup>	4

<sup>1</sup> Measured at 0 °C.

<sup>2</sup> Measured at -50 °C.

<sup>3</sup> Calculated for hydration number equal to 32.4.

ing composition were repeated many times until the metastable phases disappeared and the mixture had to be cooled to -50 to -60 °C. Using the solubility method and crystal fusion as described above it was possible to draw the metastable contin-

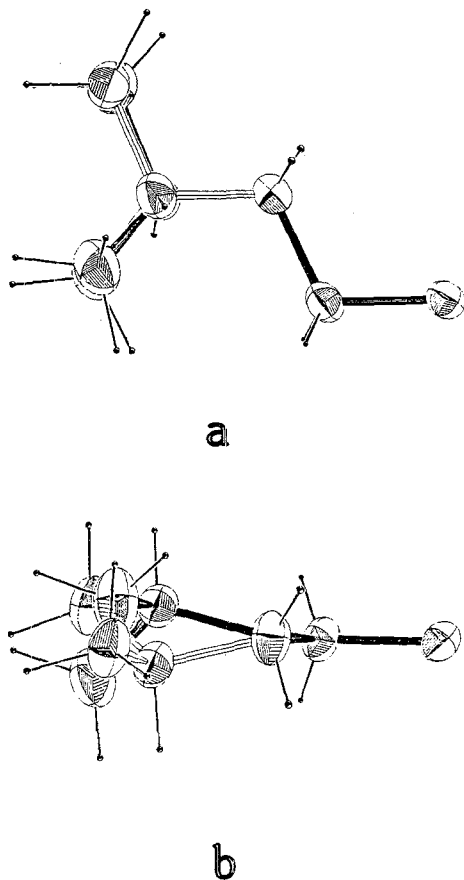


Fig. 2. Orientational disorder of the isopropyl end of the aliphatic moiety, viewed in two mutually perpendicular projections. Bonds representing the more populated orientation are shown as solid lines.

uation of the crystallization branch of this  $h_{27}$  polyhydrate for the diluted region. To grow single crystals of this compound solutions with a concentration of  $\sim 23\%$  wt. at  $25\text{--}28^\circ\text{C}$  and the crystal fusion method mentioned above were used; although under these conditions the hydrate  $h_{27}$  is metastable, transparent crystals were obtained which looked like distorted octahedra with distinct edges.

Growing  $h_{32}$  crystals was possible only in the absence of any mechanical action or stirring in a  $\sim 22\%$  wt. solution at  $18\text{--}20^\circ\text{C}$ . The crystals looked like transparent octahedral prisms with distinct edges, sometimes growing to a considerable size (about 3 cm long). Mechanical disturbance of the solution where  $h_{32}$  crystals were growing resulted in turbidity and the appearance of many tiny  $h_{38}$  crystals.

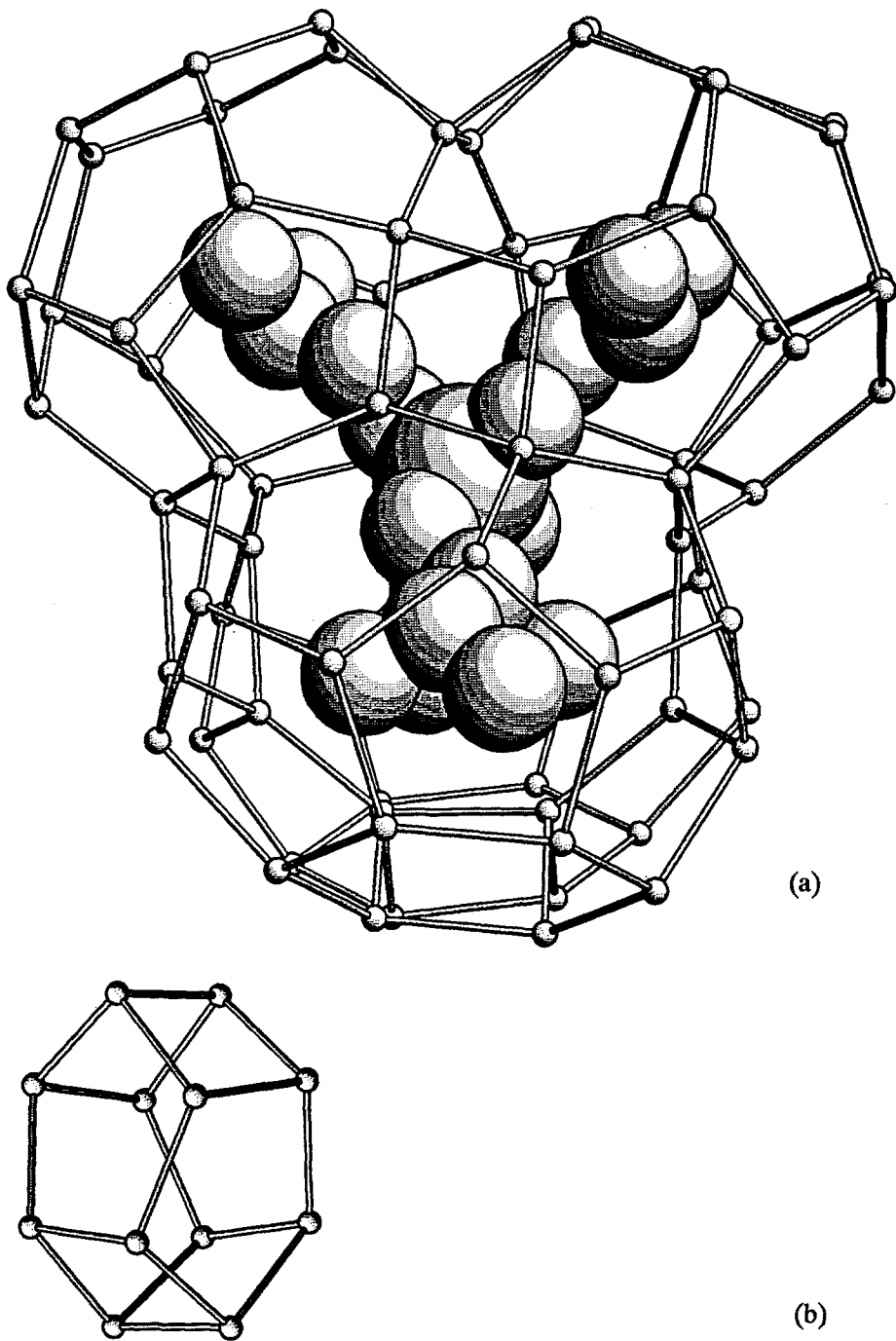


Fig. 3. (a) The cation  $(i\text{-C}_5\text{H}_{11})_4\text{N}^+$  enclosed in a four-chamber cavity as compared to (b) a  $4^4 5^4$  small cavity (hydrogen atoms are omitted). The circles represent oxygen vertex positions and the lines represent edges of hydrogen-bond length.

### 3.2. STRUCTURE

The atomic coordinates, bond distances and angles are listed in Tables III–IV. While the structure solution was rather straightforward, the refinement was not. Anisotropic thermal parameters of some of the carbon atoms in the guest cation, namely C(3), C(4) and C(5), were unexpectedly high and the geometry around C(3) did correspond to an olefinic rather than a parafinic isopropyl group [i.e. C(4)=C(3)–C(5) rather than C(4)–C(3)–C(5)]. However, a careful analytical examination of the chemicals used in the preparation of the hydrate crystals subsequently ruled out the possibility of substitution at the alkylammonium cation by an olefinic group. Next, tedious trial and error succeeded in establishing orientational disorder of the isopropyl end of the aliphatic moiety, the result being shown in Figure 2a. In refinement the hydrogen atoms bonded in C(3), C(4) and C(5) were allowed to ‘ride’ on their parent carbon atoms. The site occupation factors for the two orientations were refined at the stage of isotropic refinement and their sum was set at 1.00. The resultant values, close to 2/3 and 1/3, respectively, were kept constant during the final, anisotropic refinement. The two possible orientations of the isopropyl group are illustrated in Figure 2b; the dihedral angle between the planes C(2), C(3), C(4) and C(2'), C(3'), C(4') being equal to 98.0(6)°.

The accommodation of the guest tetraisoamylammonium cation within the host water framework is depicted in Figure 3. For the sake of clarity the higher populated orientation of the guest species is shown only.

### 4. Discussion

Three hydrates are formed in the (*i*-C<sub>5</sub>H<sub>11</sub>)<sub>4</sub>NF-water system, two of which (h<sub>38</sub> and h<sub>27</sub>) occur in stable crystallization ranges. Hydrate h<sub>27</sub> is the most thermally stable compound among the three. X-ray structural study of the single crystals of this compound has revealed a new polyhedral structure of the host framework containing two new types of cavities (idealised description): (1) a large cavity – 15-hedra 7<sup>1</sup>6<sup>3</sup>5<sup>9</sup>4<sup>2</sup>; (2) a small cavity – 8-hedra 5<sup>4</sup>4<sup>4</sup>. Two pairs of large cavities make up a four-chamber cavity. The cavities in a pair are connected by heptagons, and the two pairs are connected by four pentagons. The tetraisoamylammonium ion is located in this four-chamber cavity, its nitrogen atom replacing a hypothetical water molecule (Figure 3). The fluorine ion constitutes a part of the host framework and is thus indistinguishable from the water molecules. The small cavity remains empty.

The host structure can be described as consisting of four-chamber cavities connected by small cavities (Figure 4). The small cavity is the smallest of all the cavities discovered so far in water-anionic frameworks of the clathrate hydrates. This cavity has been found in the structure of the semiclathrate *t*-C<sub>4</sub>H<sub>9</sub>NH<sub>2</sub> · 9.75 H<sub>2</sub>O [15]. The packing coefficient [17] of this structure is equal to 0.604 at 0 °C, which exceeds the packing coefficients for clathrate polyhydrates known so far. The

TABLE III. Fractional atomic coordinates ( $\times 10^4$ ) and  $B_{\text{eq}}$  with e.s.d.s (in parentheses) for non-hydrogen atoms.\*

Atom	$x/a$	$y/b$	$z/c$	$B_{\text{eq}}$
<i>Guest</i>				
N	0	2500	1250	2.07(3)
C(1)	627(1)	2102(1)	740(1)	2.28(3)
C(2)	1026(1)	2644(1)	148(1)	2.78(3)
C(3)	1777(2)	2300(2)	-188(2)	2.50(7)
C(4)	1639(4)	2890(3)	-740(4)	4.2(1)
C(3')	1486(5)	2201(4)	-507(5)	2.7(1)
C(4')	2037(5)	1568(4)	-218(5)	3.4(1)
C(5')	1948(6)	2806(7)	-1013(6)	3.3(2)
<i>Host</i>				
O(1)	4241(1)	8828(1)	575(1)	2.84(3)
O(2)	4171(1)	2628(1)	513(1)	3.21(3)
O(3)	3195(1)	10(1)	126(1)	2.81(2)
O(4)	4102(1)	1280(1)	414(1)	2.95(3)
O(5)	2303(1)	4569(1)	1159(1)	2.93(2)
O(6)	575(1)	9569(1)	1018(1)	3.04(3)
O(7)	-788(1)	10368(1)	584(1)	3.16(3)

\* The fluoride ion is indistinguishable from the water molecules so that O(1)–O(7) account for ( $\text{F}^- + 27 \text{H}_2\text{O}$ ) in the stoichiometric formula.

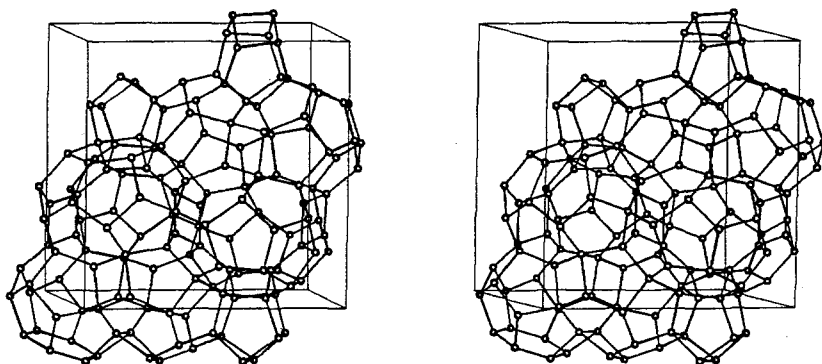


Fig. 4. Stereo view of the water-anionic host framework ( $i\text{-C}_5\text{H}_{11}$ ) $_4\text{NF} \cdot 27 \text{H}_2\text{O}$ . The circles represent oxygen vertex positions and the lines represent edges of hydrogen-bond length. The entire framework consists of four 4-chamber cavities and four 8-hedra, with centers, respectively, at sites ( $a$ ) and ( $b$ ) of  $\bar{4}$  symmetry. (Directions of crystallographic axes:  $a$  perpendicular to the drawing,  $b$  across from left to right,  $c$  up from bottom to top.)



TABLE IV. Bond distances (Å) and angles (°) with e.s.d.s (in parentheses) involving non-hydrogen atoms.

N-C(1)	1.527(1)
C(1)-C(2)	1.521(2)
C(2)-C(3)	1.511(3)
C(3)-C(4)	1.519(5)
C(3)-C(5)	1.517(7)
C(2)-C(3')	1.556(8)
C(3')-C(4')	1.50(1)
C(3')-C(5')	1.55(1)
N-C(1)-C(2)	115.1(1)
C(1)-C(2)-C(3)	113.3(1)
C(2)-C(3)-C(4)	112.4(2)
C(2)-C(3)-C(5)	110.0(3)
C(4)-C(3)-C(5)	111.0(3)
C(1)-C(2)-C(3')	114.3(2)
C(2)-C(3')-C(4')	114.5(6)
C(2)-C(3')-C(5')	109.6(6)
C(4')-C(3')-C(5')	110.1(6)

large packing coefficient of structures with vacant cavities (compare this packing coefficient with the value of 0.59 for the double hydrate  $\text{THF} \cdot 0.5(\text{C}_3\text{H}_7)_4\text{NF} \cdot 16 \text{H}_2\text{O}$  of cubic structure **II** with filled large and small cavities [16]) suggests a large complementary ability of the tetraisoamyl cation towards the large cavities of the polyhydrate  $h_{27}$  water framework.

The formation of tetragonal hydrate  $h_{32}$  is also interesting. In spite of the fact that it is completely metastable towards the other two polyhydrates in this system in the whole T,X-range studied, it is more stable than the similar tetra-*n*-butylammonium fluoride hydrate.

Figure 5 shows the phase diagrams of the water-tetra-*n*-butylammonium and water-tetraisoamylammonium fluoride systems on an equal scale. The tetragonal tetraisoamylammonium fluoride hydrate 1 : 32 (continuous line) has a m.p. 4° higher than the analogous hydrate of tetra-*n*-butylammonium fluoride. As is generally known in the tetragonal structure **I** [9, 17, 18] the ratio of the number of T-cavities to the number of P-cavities is equal to 4 (T : P = 4). Thus we can conclude that the isoamyl group stabilizes the T-cavity at least as efficiently as the *n*-butyl group. The comparison of the shape and size of these alkyl groups and the T-cavity (Figure 6) shows that the isoamyl group makes more effective use of the space of the T-cavity. Since the T-cavity is the smallest among the large ones, this conclusion is more correct for other large cavities. The phase equilibria of the system studied show the justification for this conclusion. Structures with a higher quota of 15-hedra (in the orthorhombic phase T : P = 1, and there are only

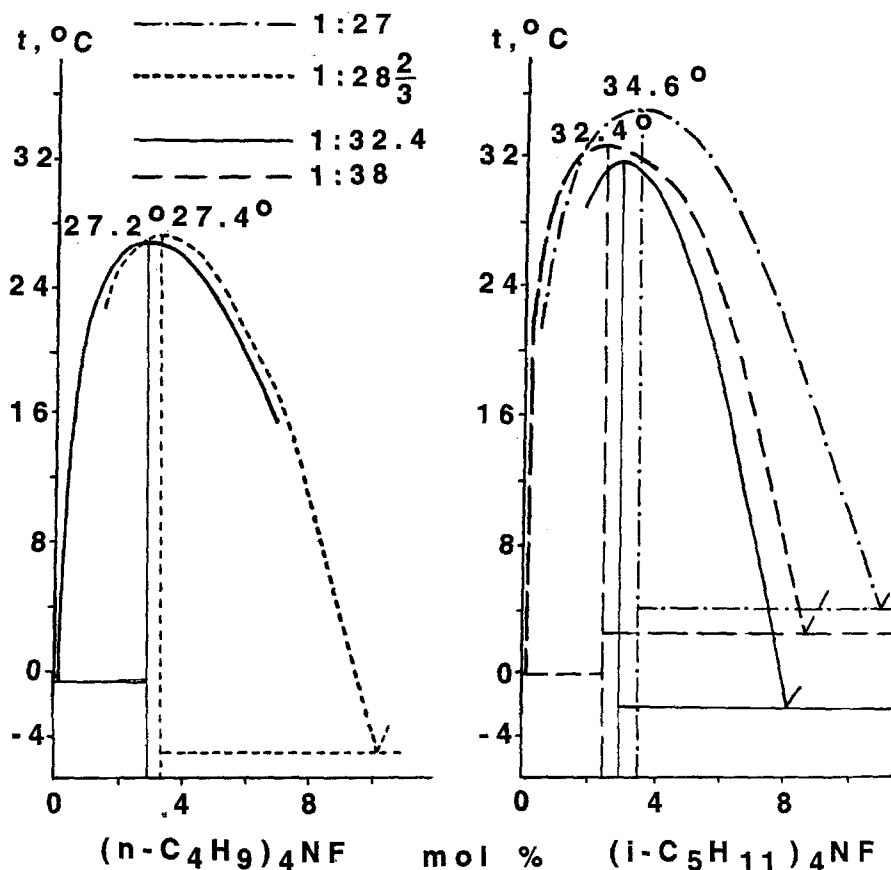


Fig. 5. Comparison of clathrate formation in the  $(n-C_4H_9)_4NF$ -water and  $(i-C_5H_{11})_4NF$ -water systems. The stable and metastable parts of the liquidus and solidus curves are shown.

15-hedra in tetragonal III [9, 17]) are more stable in the tetraisoamylammonium system, and there are no such hydrates in the tetra- $n$ -butylammonium system.

It is noted that the orthorhombic polyhydrate  $h_{38}$  exists in the  $(i-C_5H_{11})_4NF$ -water system over quite a wide concentration range of dilute solutions, and at room temperature crystals of this substance generally appear first. It is due to this behaviour that over three decades ago Feil and Jeffrey discovered only this hydrate, which is the easiest to observe [3].

In conclusion it should be noted that although this system has been studied for many years, there is no reason to claim that all possible polyhydrates have been discovered. In the crystallization range of the hydrate  $h_{27}$  we have observed some thermal effects that cannot be attributed to any one liquidus curve of the hydrates we identified. It seems likely that these effects could be due to the supercubic structure I hydrate (1 : 28.7) [9, 17], which crystallizes in the tetra- $n$ -

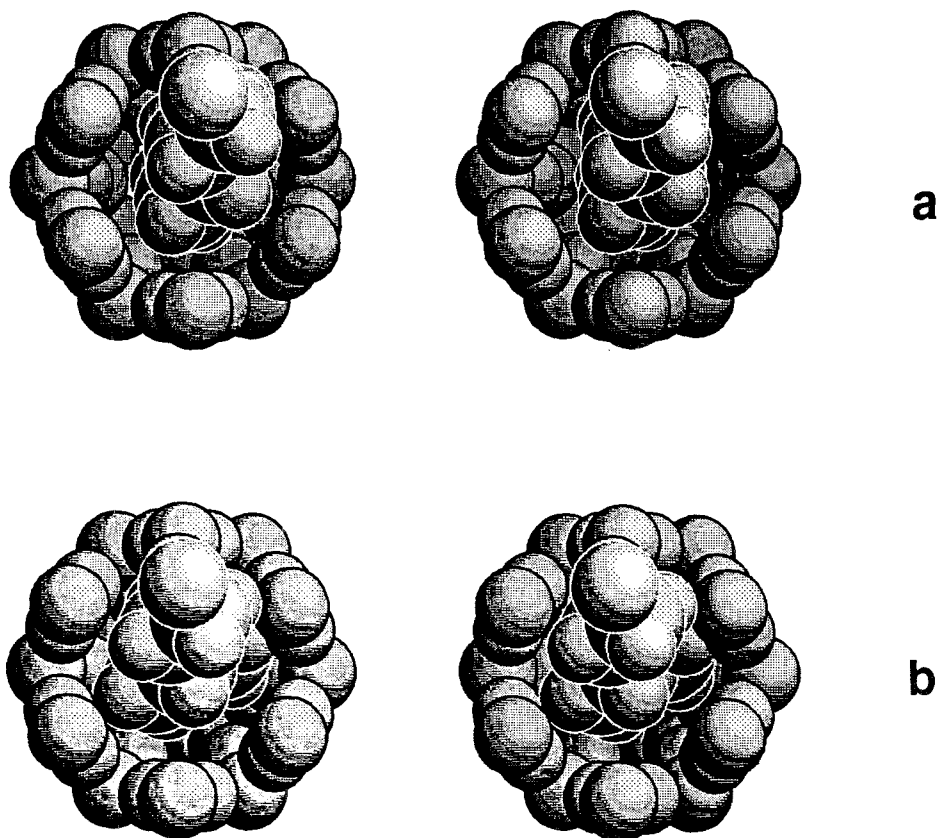


Fig. 6. The  $(n\text{-C}_4\text{H}_9)_4\text{N}^+$  (a) and  $(i\text{-C}_5\text{H}_{11})_4\text{N}^+$  (b) cation occupying a portion of the T-cavity (stereo view).

butylammonium system. T-Cavities are the only large cavities in this structure and, as shown above, the isoamyl group stabilizes them rather efficiently.

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