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Phase Diagram of the $(C_3H_7)_4NF\text{-}H_2O$ System and Crystal Structure of the Layered $(C_3H_7)_4NF\cdot 11H_2O$ Hydrate

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The phase diagram of the binary $(C_3H_7)_4NF\text{-}H_2O$ system has been studied. Three polyhydrates, $(C_3H_7)_4NF \cdot 12H_2O$, $(C_3H_7)_4NF \cdot 11.5H_2O$ and $(C_3H_7)_4NF \cdot 11H_2O$, which melt congruently at -5.1; -6.7; -7.8°C, respectively, were found in the system. A single crystal X-ray structure of the novel hydrate $Pr_4NF \cdot 11H_2O$ is reported. The space group for the layered hydrate is orthorhombic Fddd with a = 7.649(2); b = 14.920(6); c = 43.61(2)Å, z = 8, Dc = 1.077 g · cm^{-3} (t = –50°C). The layers of water and those of cations $(C_3H_7)_4N^+$ are held together by electrostatic and van der Waals interactions. Water forms a double water-fluoride layer which consists of interconnected fragments 5^4.

INTRODUCTION

Tetraalkylammonium salts with large hydrocarbon fragments, such as butyl (Bu) and isoamyl (i-Am), can form clathrate hydrates and in the process occupy four-section cavities of different configuration which consist of large cavities: T ($5^{12}6^2$**), P ($5^{12}6^3$), and H ($5^{12}6^4$).[1,2] A case is also known where one hydrocarbon fragment of the guest molecule was replaced by the propyl (Pr) fragment (Bu_3PrNF). In this case clathrate hydrates of similar structure were formed, as is the case with the $Bu_4NF\text{-}H_2O$ system. However, their melting points were considerably lower than those of the hydrates of similar structure with the guests Bu_4NF and i-Am_4NF.[3] In this paper we do not consider the influence of the anion. We discuss only the systems with tetraalkylammonium fluorides. From the previous data[2,5] it is clear that the fluoride anion distorts the water framework the least[6] which results in the maximum stability of the hydrates of tetraalkylammonium fluorides compared with the hydrates of tetraalkylammonium chlorides, bromides, and iodides. It has also been shown that the cation Pr_4N^+ can be located in the four-section cavity which consists of four adjacent pentagondodecahedra.[7] In

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**$5^{12}6^2$ descriptor means that the cavity consists of 12 pentagonal faces and 2 hexagonal faces.

this case it additionally stabilizes the water framework, forming double clathrate hydrates (e.g. $THF \cdot 0.5Pr_4NF \cdot 16H_2O$). Since the propyl fragments are small, the cation Pr_4N^+ cannot stabilize the 4-section cavities consisting of four large ones (e.g., the T_4 cavity made up of four adjacent 14-hedra $5^{12}6^2)^2$ well enough, and form the corresponding hydrates with high water content (e.g., $Pr_4NF \cdot 28H_2O$). This was corroborated by the work of Nakayama[8] who studied a part of this system. This paper deals with the study of the binary Pr_4NF–H_2O system in a wider concentration range and the X-ray structural study of one of the hydrates found in the system.

TABLE I Crystal data and summary of data collection

Compound	$(C_3H_7)_4NF \cdot 11H_2O$
Molecular mass	403.5
Space group	Fddd
Unit cell parameters	
a,Å	7.649(2)
b,Å	14.920(6)
c,Å	43.61(2)
V,Å^3	4976(1)
molecules/unit cell	8
T,°C	223
Calc.density,g· cm^{-3}	1.077
Diffractometer	CAD4 Enraf-Nonius
Radiation	graphite monochromated)Cu K_α
Max cryst dimensions, mm	0.3 × 0.4 × 0.5
2θ range, deg	4–76
No. of reflections collected	1311
No. of observed reflections	1086
Reflections observed criterion	>2sigma(I)
No. of parameters varied	92
Absorption and/or extinction correction	none
R	0.040
R for all reflections	0.048
WR2 for observed reflections	0.103
GOF for all reflections	1.038
Residual extrema in final difference map [e Å^{-3}]	–0.13 to 0.14

EXPERIMENTAL

The initial Pr_4NF—water solution was prepared by an ion exchange reaction of Pr_4NJ with AgF. Recrystallization was carried out from water solution of salt by precipitating hydrate crystals followed by concentration of the product over phosphorous pentoxide in a vacuum-drier. All the solution used were prepared from the initial solution and bidistilled water by weighing. The water content was determined by the Karl Fischer technique with the error 0.5%; the Pr_4NF content was determined by titration with sodium tetraphenylborate in the presence of a cation-selective electrode[9] (error 0.5%). Melting points and solid phase transformations were recorded by the DTA technique.

Single crystals of the hydrate $Pr_4NF \cdot 11H_2O$ were grown from water solutions (7.5% mol. of Pr_4NF). Under these conditions the solid and liquid phases were present in approximately the same proportions which favoured the growth and selection of single crystals. The solutions were rapidly cooled until crystallization began; temperature was increased to -12°C. The solution with crystals was kept at this temperature during several days; temperature was regularly made to increase so that it should be above the melting point of the crystals for several minutes which resulted in the melting of some crystals. After that temperature was decreased to –12°C. The single crystals obtained in this way had clear-cut faces and were shaped like tetragonal prisms.

The X-ray study was performed by using crystal placed in glass capillaries. A summary of the experimental data on the X-ray diffraction is given in Table I. The structure was solved by direct methods (SHELX86[10]) and refined using SHELX93.[11] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms on tetrapropylammonium cation were placed in calculated positions and those associated with the H_2O molecules were located on a difference Fourier map. Refinement converged with R = 0.040 for 1086 observed reflections. The final fractional coordinates are given in Table II and bond lengths and angles, in Tables III and IV.

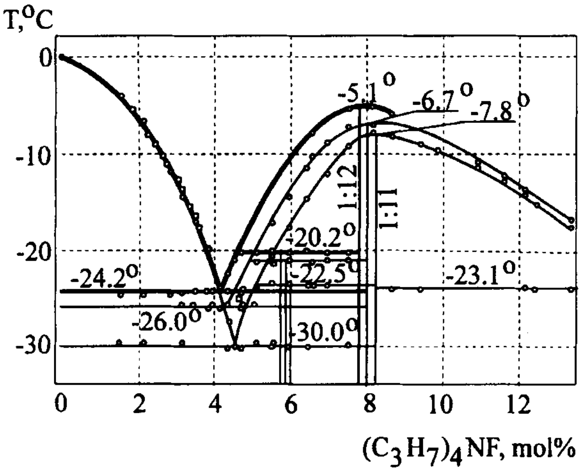

FIGURE 1 Phase diagram of the $Pr_4NF–H_2O$ system (O–our data, □–data of Nakayama). The thick lines show stable liquidus lines, and the thin lines, metastable ones.

RESULTS AND DISCUSSION

The phase diagram of the $Pr_4NF–H_2O$ system is shown in Figure 1. As is seen from the Figure our results are in good agreement with those of Nakayama[6] (his experimental points are plotted on the diagram). No hydrates with high (more than 18 water molecules per one molecule of Pr_4NF) water content form in the system. Three hydrates of similar composition which melt congruently were found in the system. The hydrate $Pr_4NF \cdot 12H_2O$ which melts at –5.1°C contains the largest amount of water. The other two hydrates, $Pr_4NF \cdot 11.5H_2O$, and $Pr_4NF \cdot 11H_2O$ melting congruently, contain even less water and melt at a temperature of –6.7°C and –7.8°C, respectively. Comparatively small number of water molecules in the hydrates suggests that clathrate hydrates of cage-like structure in which the cations Pr_4N^+ would be accommodated in isolated cavities are unlikely to form. Exothermal effects on the phase diagram corresponding to –20.2, –21.2 and –22.5°C can be accounted for by incongruent melting of the hydrates assumed to be of the composition $Pr_4NF \cdot 16(2)H_2O$. The eutectic mixture of water and the hydrate $Pr_4NF \cdot 12H_2O$ melts at -24.2°C, that of water and the hydrate $Pr_4NF \cdot 11.5H_2O$, at –26.0°C, and that of water and the hydrate $Pr_4NF \cdot 11H_2O$, at –30.0°C. The effect observed at –23.1°C corresponds to the melting of the eutectic mixture of the metastable hydrate $Pr_4NF \cdot 11H_2O$ with enhydrous Pr_4NF.

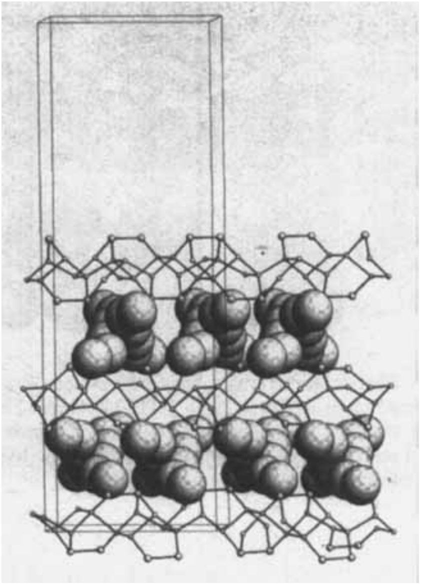

FIGURE 2 Plot of the arrangement of the cations Pr_4N^+ and water-fluoride layers in the $Pr_4NF \cdot 11H_2O$ hydrate. Positions of fluoride atoms (25% probability) in water-fluoride layers are marked with large balls. View approximately along the *a* axis (hydrogen atoms are omitted).

We succeeded in growing single crystals of the metastable hydrate $Pr_4NF \cdot 11H_2O$. Although this hydrate has no stable range of existence it appeared possible to obtain its crystals due to kinetic difficulties this hydrate has to overcome when it changes to the more stable hydrate $Pr_4NF \cdot 11.5H_2O$ or to the stable hydrate $Pr_4NF \cdot 12H_2O$.

The X-ray analysis showed the hydrate $Pr_4NF \cdot 11H_2O$ to be of layered structure (Figures 2,3). The final fractional coordinates are presented in Table II and bond lengths and angles, in Tables III and IV. Pinacol hexahydrate[12], 2,5-dimethil-2,5-hexanediol tetrahydrate[13], and 2,7-dimethyl-2,7-octanediol tetrahydrate[14] have also been shown to be of layered structure. In all of these hydrates

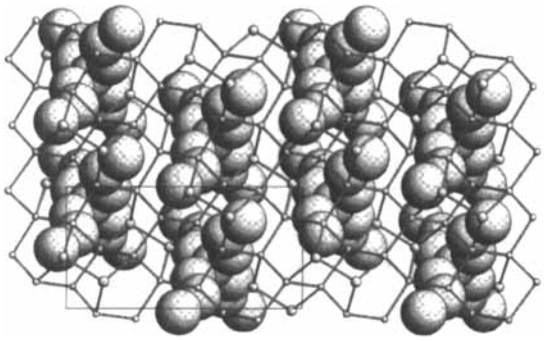

FIGURE 3 Plot of the arrangement of the cations Pr_4N^+ and water-fluoride layer in the $Pr_4NF \cdot 11H_2O$ hydrate. Positions of fluoride atoms (25% probability) in water-fluoride layers are marked with large balls. View along the *c* axis (hydrogen atoms are omitted).

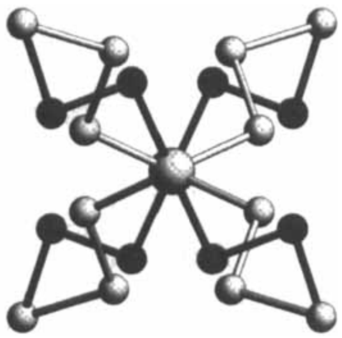

FIGURE 4 Orientational disorder of the propyl fragments of the Pr_4N^+ cation. Positions of C1, C2, and C3 atoms are marked with white balls and those of C1', and C2' atoms, with black ones (hydrogen atoms are omitted).

water forms crimp layers which consist of distorted pentagons. Pinacol and diol molecules also form layers connected with water layers by hydrogen bonds. The hydrate $Pr_4NF \cdot 11H_2O$ studied by us is different from the layered pinacol and diol hydrates. First, the layers of water and cations Pr_4N^+ are held together by electrostatic and van der Waals interaction rather than by hydrogen bonding. The minimum distance O2/F....C1 is equal to 3.40 Å, O2/F....C2, to 3.63 Å, and O2/F....C3, to 3.88 Å. Second, in the hydrate $Pr_4NF \cdot 11H_2O$ water forms a double water-fluoride layer which consists of interconnected fragments 5^4 (Figure 5) rather than a monolayer, as is the case with the pinacol and diol layered hydrates. This fragment might be visualized as a hypothetic cavity with non-plane faces (Figure 6). However, the inner diameter of this kind of cavities is already too short, and these cavities cannot accommodate even such small molecules as He.

TABLE II Fractional atomic coordinates for non-hydrogen atoms

Atom	x/a	y/b	z/c	U_{eq}
O1	0.0226(2)	0.8197(1)	0.2706(1)	0.040(1)
O2/F[a]	0.0317(1)	0.2051(1)	0.4413(1)	0.038(1)
O3	0.0244(1)	0.3271(1)	0.2346(1)	0.038(1)
N	0.1250	0.1250	0.1250	0.025(1)
C1	0.0194(2)	0.0486(1)	0.1130(1)	0.027(1)
C2	−0.1182(2)	0.0736(1)	0.0897(1)	0.045(1)
C3	−0.2350(2)	−0.0060(1)	0.0814(1)	0.044(1)
C1′	0.2453	0.1603	0.0989	0.028
C2′	−0.1290(4)	0.0194(2)	0.1080(1)	0.041(1)

[a] The fluoride ion is statistically disordered, occupying the position of the water oxygen atom O2 with a probability of 0.25.

The carbon atoms (C1 and C2) of the propyl fragment of the cations that are closely packed in the layers are disordered with a probability of 0.5 between two positions (Figure 4).

Fluoride ions in the water-fluoride layer are statistically distributed between four positions with a probability of 0.25. Because of electrical interaction a fluoride ion should occupy the position nearest to the nitrogen atom of the cation Pr_4N^+. Electrostatic interaction and conditions of the best packing make the anion F^- (or the atom O2 of water oxygen) take up a position closer to the C1 atom than to the C2 one and the more so as the C3 atom of the carbon fragment.

The water-anion layers consist of distorted pentagons. The lengths of the hydrogen bonds Ow...Ow between water molecules are equal to 2.69–2.80 Å, and those of the hydrogen bonds Ow...Ow...Ow, to 89–142° (Table IV). This considerable difference in the angles between the hydrogen bonds and the ideal tetrahedral ones can

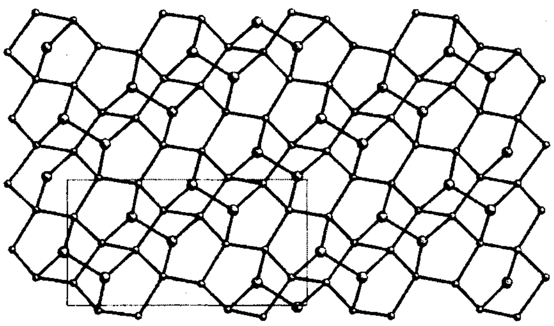

FIGURE 5 Water-fluoride layer of the $Pr_4NF \cdot 11H_2O$ hydrate. View along the *c* axis. Positions of fluoride atoms (25% probability) are marked with large balls (hydrogen atoms are omitted).

partially account for the low stability and melting point of the hydrate $Pr_4NF \cdot 11H_2O$.

Hydrogen atoms of the water molecules were located on a difference Fourier map. They are disordered, occupying all possible sites in the water-anion framework.

The calculated density of the studied hydrate is 1.077 g.cm^{-3} (–50°C) which is less than that of the hydrate i-$Am_4NF \cdot 27H_2O$ (1.093 g·cm^{-3}, –5°C)[15] with the vacant cavities $5^4 4^4$ and somewhat larger than that of the tetragonal hydrate i-$Am_4NF \cdot 32.4H_2O$ (1.066 g·cm^{-3}, –5°C)[15] with vacant dodecahedral cavities. The packing coefficient of the hydrate $Pr_4NF \cdot 11H_2O$ ($k = 0.598$) and the experimental dependence dT/dP of the melting of the hydrates on k[8] allows us to predict with certainty that this hydrate will be stabilized by pressure.

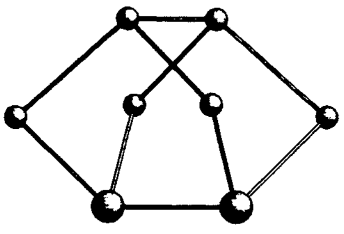

FIGURE 6 Fragment 5^4 of water-fluoride layer (hydrogen atoms are omitted). Positions of fluoride atoms (25% probability) are marked with large balls.

TABLE III Bond distances (Å) and angles (°) involving non-hydrogen atoms

N-C1	1.492(1)
C1-C2	1.510
C2-C3	1.530
N-C1′	1.560
C1′-C2′	1.518(3)
C1′-N-C1′	107.5
N-C1-C2	115.1(1)
C1-C2-C3	112.0
N-C1′-C2′	116.2(1)
C1′-C2′-C3′	110.2(1)

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TABLE IV Hydrogen bond distances (Å) and angles (°) in water-anion framework involving non-hydrogen atoms

O1...O1	2.799
O1...O2	2.814
O1...O3	2.691
O2...O3	2.765
O2...O2	2.787
O3...O3	2.687
O1...O1...O2	142.1
O1...O1...O3	97.3
O1...O1...O1	110.1
O2...O1...O3	112.5
O2...O1...O1	89.6
O3...O2...O1	94.7
O3...O2...O2	102.5
O1...O2...O2	104.2
O2...O3...O3	134.0
O2...O3...O3	106.8
O2...O3...O1	94.9
O3...O3...O3	109.7
O3...O3...O1	100.7
O3...O3...O1	106.3

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