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Channel polyhydrate $(C_2H_5)_4NF{\cdot}11H_2O$

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The phase diagram of the system $(C_2H_5)_4NF–H_2O$, has been studied. The polyhydrates $(C_2H_5)_4NF{\cdot}5H_2O$ and $(C_2H_5)_4NF{\cdot}11H_2O$, which melt congruently at 24.8 and −13.6 °C respectively, have been found in this system. The hydrate $(C_2H_5)_4NF{\cdot}11H_2O$ has a channel–cavity structure. Water and fluoride anions form a three-dimensional framework consisting of channels and cavities. The channels are filled with cations $(C_2H_5)_4N^+$, and the cavities are vacant. The polyhydrate $(C_2H_5)_4NF{\cdot}11H_2O$ has the following crystallographic parameters: $a = 12.393(3)$, $b = 22.595(7)$ $c = 11.483(3)$ A ($T = -100$ °C), space group *Pnnm*, $Z = 6$.

Until recently it was believed that clathrate hydrates can be formed only by those peralkylonium salts that contain butyl and isoamyl fragments.[1] The existence of tetramethylammonium hydroxide clathrate pentahydrate[2] and the double clathrate hydrate $(CH_3)_4NF{\cdot}0.5(C_3H_7)_4NF{\cdot}15H_2O$[3] could be considered an exception to this rule. It turned out that the cations Me_4N^+ can stabilize water-anion frameworks, occupying one cavity rather than four adjacent ones as is the case with tetrabutylammonium and tetraisoamylammonium cations.[1] The absence of reports on hydrates with larger hydrate numbers in the systems tetraethylammonium fluoride–water and tetrapropylammonium fluoride–water has favoured the opinion that cations like tetraethyl- and tetrapropylammonium cannot stabilize any water frameworks. Earlier we studied the propylammonium fluoride–water system where we first observed a layered polyhydrate of the composition $(C_3H_7)_4NF{\cdot}11H_2O$.[4] We report here the observation of polyhydrates in the $(C_2H_5)_4NF–H_2O$ system.

We studied the system by DTA in the concentration range 0 to 20 mol % of tetraethylammonium fluoride solutions, obtained hydrates and determined their composition. Figure 1 shows part of the studied diagram of the system $(C_2H_5)_4NF–H_2O$, where the two hydrates $(C_2H_5)_4NF{\cdot}5H_2O$ and $(C_2H_5)_4NF{\cdot}11H_2O$ form, melting congruently at 24.8 and −13.6 °C, respectively. The hydrate we discuss in this paper is of the composition $(C_2H_5)_4NF{\cdot}11H_2O$. The hydrate crystals exist in equilibrium with an aqueous solution in a very narrow temperature and concentration range: from −27 to −13.7 °C and from 5.3 to 10.6 mol% of Et_4NF, respectively. Analysis of the hydrate crystals for water content by Fisher's technique resulted in the composition $(C_2H_5)_4NF{\cdot}10.97(5)H_2O$ (in brackets we give the standard deviation for five independent measurements). Using the phase diagram data we grew single crystals of this hydrate from water solutions containing 7.5 mol% of Et_4NF at −20 °C. Under these conditions the solid and liquid phases were present in approximately the same proportions which favoured the growth and selection of single crystals. After an hour transparent, well-defined rectangular prisms of the hydrate $(C_2H_5)_4NF{\cdot}11H_2O$ were formed from solution. A single crystal of the hydrate was placed in a thin-wall glass capillary and analysed by X-ray crystallography. We carried out the analysis on a Cad-4 diffractometer, using Cu Kα radiation and a graphite monochromator. The unit cell of the studied hydrate has the following parameters: $a = 12.393(3)$, $b = 22.595(7)$, $c = 11.483(3)$ A ($T = -100$ °C), the space group *Pnnm* and $Z = 6$. Solvation and refinement of the structure was carried out with the help of the programs SHELX-86 and SHELX-93.[5,6] For the 2573 [$I > 4\sigma(I)$] reflections observed (3571 total) the structure was refined to $R = 0.061$. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms in ethylammonium cation were placed in calculated positions and those associated with the H_2O molecules were located on a difference Fourier map. The hydrogen atoms of the water molecule are disordered, occupying all possible sites in the water–anion framework.

The structure of the clathrate hydrate we observed has channels and cavities (Figure 2). The channels along the x axis

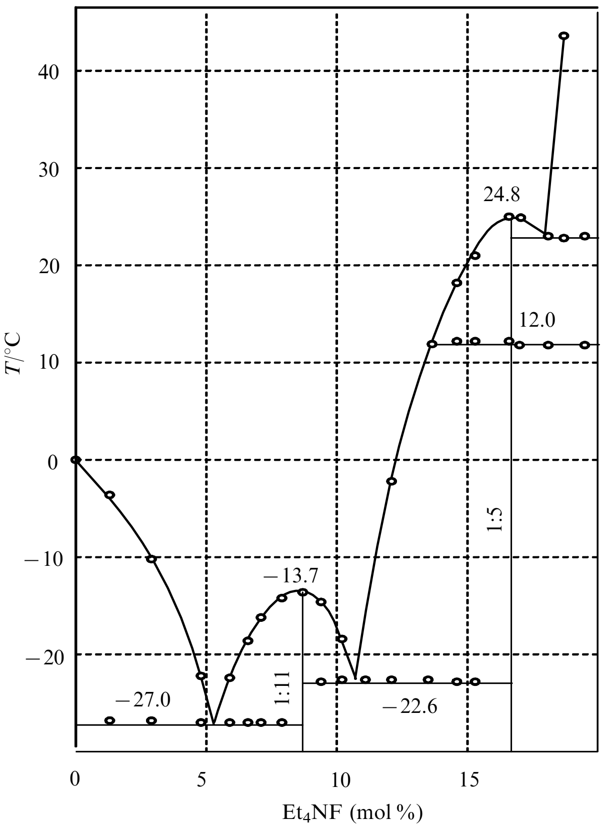

Figure 1 The phase diagram of the system $(C_2H_5)_4NF–H_2O$.

are filled with cations $(C_2H_5)_4N^+$, the narrow part of the channel being occupied by one cation and the broad part by two cations (Figure 3). The cavities 4^25^8 found earlier in the structure of the hydrates $(i\text{-}C_5H_{11})_4PBr{\cdot}32H_2O$[7] and $(CH_3)_4NOH{\cdot}7.5H_2O$ (β-phase)[2] are vacant. The cavities adjoin the square sides, forming columns situated along the *x* axis. The diameter of the small vacant inner cavity, 4^25^8, is equal to 3.23 A and the cavity can be occupied only by He and H_2 molecules. Earlier we showed that the pentagondodecahedral cavities in cubic structures of clathrate hydrates can accommodate He molecules.[8] The cavity 4^25^8 is more suitable for the inclusion of He molecules since its size corresponds better to the size of a guest He molecule.

The fluoride anions are statistically disordered; they substitute for the water molecules in the framework and form a water–anion framework. The framework is made up of pentagons, hexagons and squares. The lengths of the hydrogen bonds $O_w{\cdots}O_w$ vary from 2.66 to 2.79 A, and the angles $O_w{\cdots}O_w{\cdots}O_w$ between the hydrogen bonds in the water framework vary from 92.5 to 133.7°. Thus, the requirements of the tetrahedral arrangement of the hydrogen bonds in water molecules are not met sufficiently. This and the presence of the vacant cavities account for the relatively low melting point of the hydrate $(C_2H_5)_4NF{\cdot}11H_2O$.

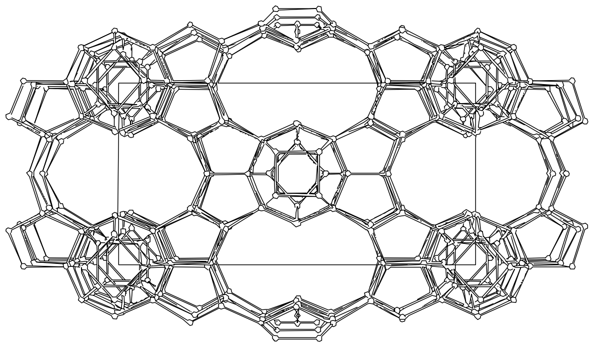

Figure 2 The water–anion framework of the hydrate $(C_2H_5)_4NF{\cdot}11H_2O$ as viewed approximately along the *x* axis. (Hydrogen atoms are omitted).

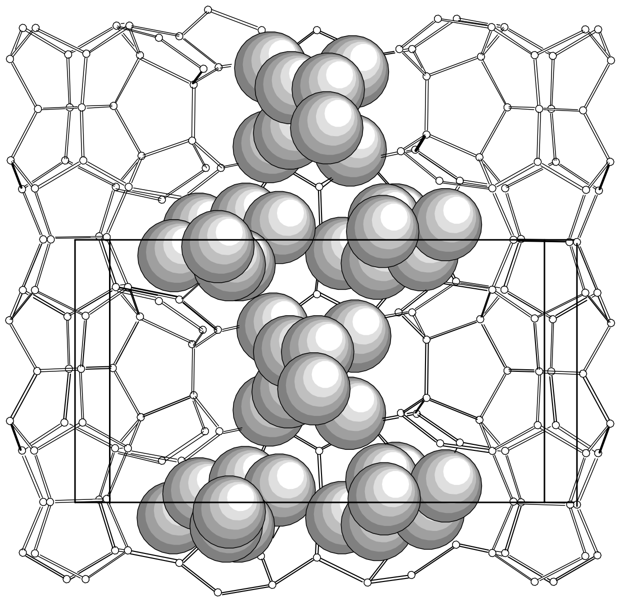

Figure 3 Channels filled with cations $(C_2H_5)_4N^+$ as viewed approximately along the *y* axis. (Hydrogen atoms are omitted).

In conclusion it should be mentioned that this is the first time that a clathrate polyhydrate whose structure contains both channels and cavities has been found.

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References

1 Yu. A. Dyadin and K. A. Udachin, *Zh. Strukt. Khim.,* 1987, **28**, 75 [*J. Struct. Chem.* (*Engl. Tranls.*), 1987, **28**, 394].
2 D. Moots and R. Seidel, *J. Inclusion Phenom.,* 1990, **8**, 139.
3 K. A. Udachin, Yu. A. Dyadin and J. Lipkowski, *Mendeleev Commun.,* 1995, 97.
4 J. Lipkowski, R. Lyuboradzki, K. A. Udachin and Yu. A. Dyadin, *J. Inclusion Phenom.,* 1992, **13**, 347.
5 G. M. Sheldrick, *Acta Crystallogr., Sect. A,* 1990, **46**, 467.
6 G. M. Sheldrick, *Acta Crystallogr., Sect. A,* 1993, **49**, (Suppl.) C53.
7 S. F. Solodovnikov, T. M. Polyanskaya, V. I. Alekseev, L. S. Aladko, Y. A. Dyadin and V. V. Bakakin, *Kristallografiya,* 1982, **27**, 247 [*Crystallography USSR* (*Engl. Tranls.*), 1982, **27**, 151].
8 K. A. Udachin, J. Lipkowski and M. Tkacz, *Supramolecular Chem.,* 1994, **3**, 181.

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