Layered polyhydrate 18-crown-6·12H_2O

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A single crystal X-ray structure of the novel layered hydrate 18-crown-6·12H_2O with the following crystallographic parameters: $a = 9.385(2)$, $b = 7.399(1)$ $c = 19.437(4)$, $\beta = 93.29(3)$ ($T = -100$ °C), space group *Pn*, $Z = 2$, $\rho_{calc} = 1.184$ g cm^{-3}, is reported.

Water is able to build various frameworks: from classic cell[1,2] and channel type[3] to layered[4–6] hydrates and even individual chains[7] from water molecules connected by hydrogen bonds. In all these compounds water can either form hydrogen bonds with the guest molecules[5,6] or interaction between them is restricted to van der Waals[8] (and, sometimes, electrostatic[3,4,9]) interactions. The type of hydrate water framework is largely determined by the number of water molecules per one guest molecule. The greater the number of water molecules, the more complex the framework formed by water. The previous study revealed that 1,10-diaza-18-crown-6 formed a polyhydrate of clathrate type.[10] We decided to learn whether crown ether 18-crown-6 could form polyhydrates. Given the ability of the crown ether 18-crown-6 to dissolve in water even better than 1,10-diaza-18-crown-6, one would expect it to form a greater variety of polyhydrates. Our study of the phase diagram of the system 18-crown-6 – H_2O was aimed at finding polyhydrates.

We studied the system 18-crown-6 – H_2O by DTA in the concentration range 0–100 mol% of 18-crown-6 aqueous solutions, obtained hydrates and determined their composition. Figure 1 shows the diagram studied for the system 18-crown-6 – H_2O, in which three hydrates form, 18-crown-6·6H_2O, 18-crown-6·8.25H_2O, and 18-crown-6·12H_2O. The hydrate 18-crown-6·6H_2O melts congruently at 23.6 °C and the hydrates 18-crown-6·8.25H_2O and 18-crown-6·12H_2O melt incongruently at 18.6 °C and 11.6 °C, respectively. The hydrate we discuss in this paper is of the composition 18-crown-6·12H_2O. The hydrate crystals exist in equilibrium with an aqueous solution in a very narrow temperature and concentration range: from −2.4 to 11.7 °C and from 4.0 to 7.7 mol% of 18-crown-6, respectively. Analysis of the hydrate crystals for water content by Fischer's technique resulted in the composition 18-crown-6·12.02H_2O (in brackets we give the standard deviation for six independent measurements). Using the phase diagram data we grew single crystals of this hydrate from water solutions containing 5.5 mol% of 18-crown-6 at 5 °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 in solution, transparent well-edged single crystals of the hydrate 18-crown-6·12H_2O formed.

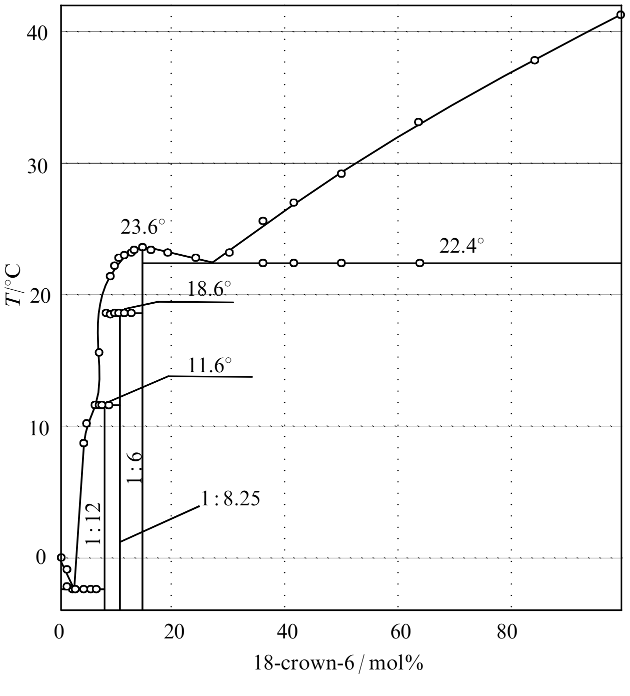

Figure 1 Phase diagram of the system 18-crown-6 – H_2O.

A single crystal of the hydrate was placed into a thin-wall glass capillary and analysed by the X-ray technique. We carried out the experiment on a Cad-4 diffractometer, using CuK_α radiation and a graphite monochromator. The unit cell of the studied hydrate has the following parameters: $a = 9.385(2)$, $b = 7.399(1)$ $c = 19.437(4)$, $\beta = 93.29(3)$ ($T = -100$°C), space group *Pn*, $Z = 2$, $\rho_{calc} = 1.184$ g cm^{-3}. Solvation and refinement of the structure was carried out with the help of the programs SHELX-86 and SHELX-93.[11,12] For 2702 [$I > 4\sigma(I)$] observed (2917 total) reflections the structure was refined to $R = 0.058$. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms on crown ether were placed in calculated positions and those associated with the H_2O molecules were located on a difference Fourier map.

The hydrate 18-crown-6·12H_2O is of a layered structure. Water molecules connected with one another by hydrogen bonds, forming pentagons and hexagons, make up layers (Figure 2). Crown ether molecules are situated between water layers, forming hydrogen bonds with water molecules of the layers (Figure 3). Crown ether molecules construct hydrogen bonds between the atoms O1, O7 and O13 and two water molecules of one water layer and between O4, O10 and O16 and two water molecules of another water layer. One water molecule on each side forms two hydrogen bonds with the crown ether molecule, the other, one hydrogen bond. Therefore, all the oxygen atoms are involved in the formation of hydrogen bonds, and the shape of the molecule is different from that of the free crown ether ellipsoid molecule with two methylene groups turned inside (conformation C_i).[13] Instead it resembles a ring of conformation D_{3d}. Previous studies by molecular dynamics simulations[14,15] of 18-crown-6 uncomplexed in water led to the conclusion that dissolution of the crystal should lead to conformational changes from C_i to D_{3d}.

Water layers are made up of pentagons and hexagons. The lengths of the hydrogen bonds $O_w \cdots O_w$ vary from 2.74 to 2.84 A, and the angles $O_w \cdots O_w \cdots O_w$ between the hydrogen bonds in the water framework vary from 94.2 to 125.0°. Thus, the requirements of the tetrahedral arrangement of the hydrogen bonds in water molecules are met sufficiently. This partially accounts for a relatively high (in comparison with

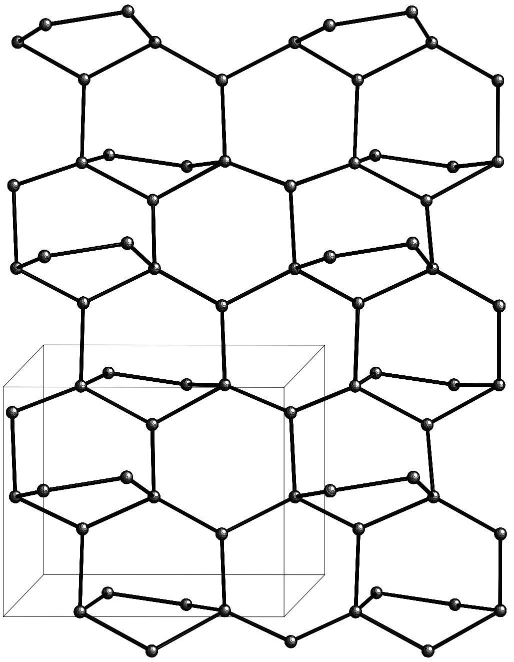

Figure 2 Water layer of the 18-crown-6·12H_2O hydrate as viewed approximately along the axis *z* (hydrogen atoms are omitted).

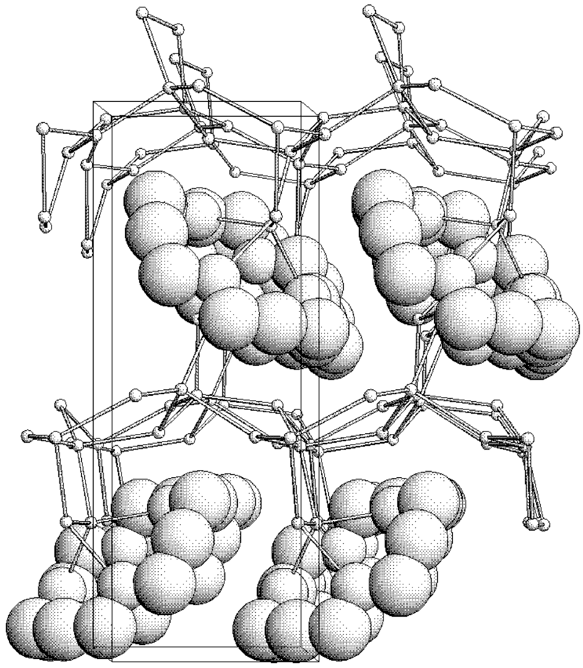

Figure 3 Plot of the arrangement of the molecules 18-crown-6 and water layers in the 18-crown-6·12H_2O hydrate viewed approximately along the *x* axis (hydrogen atoms are omitted).

other polyhydrates) melting point of the hydrate 18-crown-6·12H_2O, which would be even higher if the crystallization field of the hydrate were not overlapped by the crystallization fields of the hydrates 18-crown-6·8.25H_2O and 18-crown-6·6H_2O.

In conclusion, it should be mentioned that this is the first time that a layered polyhydrate of crown ether has been found.

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