Layered polyhydrate 15-crown-5·8H_2O

Konstantin A. Udachin*[a] and Janusz Lipkowski[b]

[a] *Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation. Fax: +7 3832 355 960; e-mail: kuku@che.nsk.su*
[b] *Institute of Physical Chemistry, Polish Academy of Sciences, 01 224 Warsaw, Poland. Fax: +4822 325 276; e-mail: klatrat@alfa.ichf.edu.pl*

The phase diagram of the system 15-crown-5–H_2O, has been studied, and the polyhydrate 15-crown-5·8H_2O, which melts congruently at 12.8 °C, has been found; a single crystal X-ray structure of the novel layered polyhydrate 15-crown-5·8H_2O is reported, which shows that water molecules connected *via* hydrogen bonds, forming pentagons and octagons make up layers, and the crown ether molecules are situated between water layers, forming hydrogen bonds with water molecules of the layers.

Water can build various frameworks in crystalline hydrates. The structure of a water framework is determined to a large extent by the nature of the hydrate-forming component. Most of the known crown ether hydrates and their complexes are compounds with one or two water molecules per crown ether molecule.[1,2] This amount of water is not sufficient for the formation of a framework, and water in this kind of compound is in the form of separate molecules connected with the crown ether complexes by hydrogen bonds. Sometimes water can be included within the crown ether cavity as an ion, H_3O^+,[3,4] or as an individual molecule.[5,6] In previous studies[7,8] we showed that the crown ethers 1,10-diaza-18-crown-6 and 18-crown-6 can form polyhydrates whose melting points are above 0 °C. In these polyhydrates water either builds a three-dimensional framework with the cavities accommodating four crown ether molecules each,[7] or a layered framework is formed where the crown ether molecules are located between the water layers.[8] No polyhydrates of the crown ether 15-crown-5 have been found so far even though its high solubility in water suggests their existence. In order to observe the 15-crown-5 polyhydrates we have studied the phase diagram of the system 15-crown-5–H_2O.

The phase diagram was studied using differential thermal analysis (DTA) technique, and the hydrate 15-crown-5·8H_2O which melted congruently at 12.8 °C was obtained (Figure 1). The polyhydrate crystals exist in equilibrium with an aqueous solution over a wide temperature and concentration range: from −34.4 to 12.8 °C and from 3.0 to 82.0 mol% of 15-crown-5, respectively. Using the phase diagram data we grew single crystals of this hydrate from water solutions containing 10 mol% of 15-crown-5 at 10 °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 a day, transparent well-edged prisms of the hydrate 15-crown-5·8H_2O had formed in the solution. Analysis of the hydrate for water content by Fisher's technique[9] gave the composition 15-crown-5·7.97(4)H_2O (in parentheses we give the standard deviation for five independent measurements). The polyhydrate single crystal was placed into a thin-walled glass capillary and analysed by the X-ray crystallography. We carried out the experiment on a Cad-4 diffractometer, using CuKα radiation and a graphite monochromator. The unit cell of the hydrate studied has the following crystallographic parameters: $a = 19.640(4)$, $b = 6.986(1)$, $c = 28.950(6)$ A, $\beta = 102.02(3)°$ ($T = -100$ °C), and the space group is $P2_1/n$, $Z = 8$, $\rho_{calc.} = 1.246$ g cm^{-3}. Solvation and refinement of the structure was carried out with the help of the programs SHELX-86 and SHELX-93.[10,11] For 6815 [$I > 4\sigma(I)$] observed (8183 total) reflections the structure was refined to $R = 0.049$. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms on the crown ether were placed in calculated positions and those associated with the H_2O molecules were located on a difference Fourier map.

The hydrate 15-crown-5·8H_2O has a layered structure in which water molecules are connected with one another by hydrogen bonds, forming distorted pentagons and octagons which make up layers with terminal water molecules on both sides of the layers (Figure 2). Crown ether molecules are situated between the water layers, forming hydrogen bonds with water molecules of the layers (Figure 3). Crown ether molecules construct hydrogen bonds between the atoms O-1 and O-10 and a terminal water molecule of one water layer, and between O-7 and O-13 and a terminal water molecule of another water layer. Half of the crown ether molecules have hydrogen bonds between the oxygen atom O-4 and water molecules of the layer. The length of the hydrogen bond O-4···O_w is 2.80 A. For the other half of the crown ether molecules the minimum distance O-4···O_w is 3.46 A. All the oxygen atoms of the crown ether molecule are planar to within 0.33 A, and the oxygen atoms of the terminal water molecules nearest to the plane are 2.08–2.45 A from the plane.

The water layers are made up of distorted pentagons and octagons. The lengths of the hydrogen bonds $O_w\cdots O_w$ vary from 2.70 to 2.88 A, and the angles $O_w\cdots O_w\cdots O_w$ between the hydrogen bonds in the water framework vary from 90.8 to 150.7°. Thus, the requirements of the tetrahedral arrangement

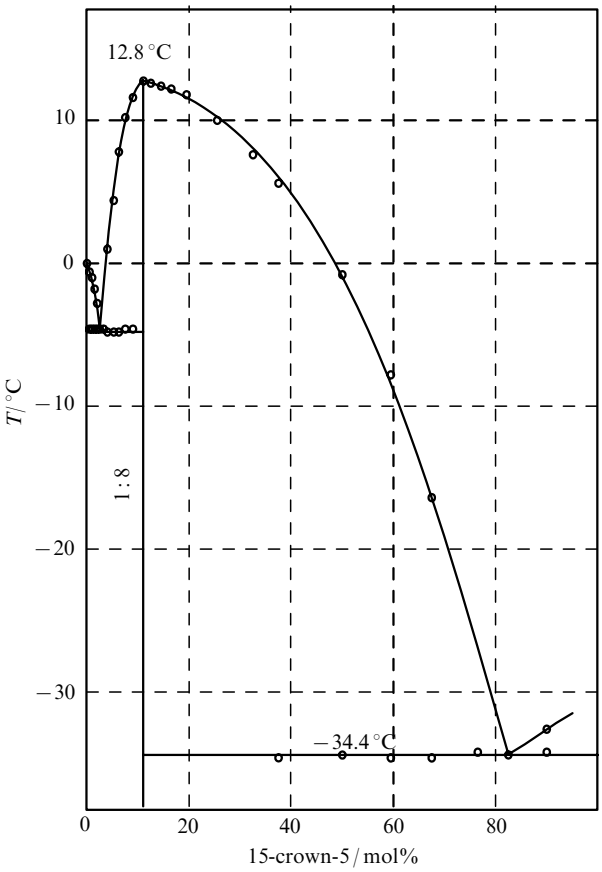

Figure 1 Phase diagram for the system 15-crown-5–H_2O.

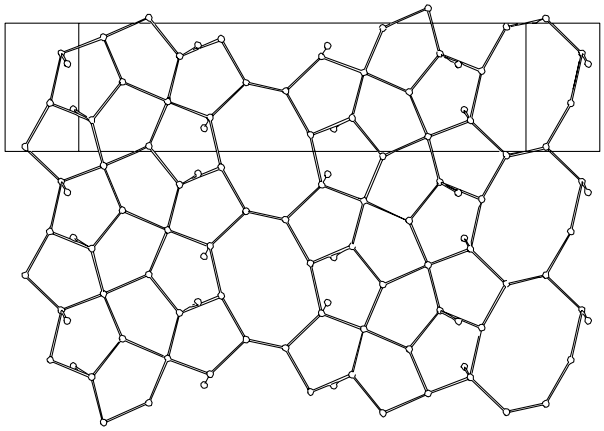

Figure 2 Water layer of the 15-crown-5·8H_2O hydrate as viewed approximately along the *x* axis (hydrogen atoms are omitted).

of the hydrogen bonds in water molecules are not met sufficiently. This partially accounts for the relatively low (in comparison with other polyhydrates) melting point of the hydrate 15-crown-5·8H_2O.

In conclusion it should be mentioned that this is the first time that a polyhydrate of crown ether 15-crown-5 has been found.

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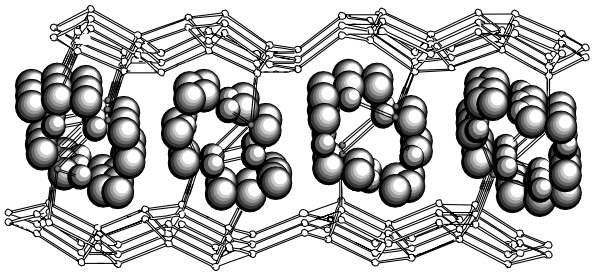

Figure 3 Plot of the arrangement of the molecules 15-crown-5 and water layers in the 15-crown-5·8H_2O hydrate as viewed approximately along the *y* axis (hydrogen atoms are omitted).

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