Clathrate Hydrates in the Water–Tetrahydropyran System at High Pressure

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Tetrahydropyran (THP) forms a clathrate hydrate $THP\cdot17H_2O$ of cubic structure II which melts at $P = 1$ atm, $T = -0.8$ °C decomposing into two liquids with an upper consolute temperature of dissolution of 226 °C. It is destabilized by pressure and at $P > 1.15$ kbar, $T = -4.3$ °C cubic structure I hydrate appears to become stable.

Cyclic ether hydrates attract interest due to the ability of the lower members of the homologuous series from ethylene oxide (EO) to tetrahydrofuran (THF) and dioxanes (DXs) to form clathrate hydrates. EO forms only a hydrate of cubic structure I (CS-I)[1] and THF, 1,3-dioxolane and dioxanes form hydrates of cubic structure II (CS-II) under 1 atm pressure. Trimethylene oxide (TMO), whose molecules are of intermediate size, forms hydrates of both structures which are, however, the least thermally stable.[2,3] The molecule of 1,4-dioxane is already sufficiently large for the H-cavity[†] and the $1,4\text{-}DX\cdot17H_2O$ hydrate is therefore less stable (incongruent melting temperature is −11.3 °C) than the $THF\cdot17H_2O$ hydrate (+4.3 °C).[2] The CS-II hydrate that is formed under normal pressure in all of the systems studied[1–4] changes under the influence of pressure to a hydrate with stoichiometry of *ca.* 1:7 (guest:water). There are good reasons to consider that this is a CS-I hydrate,[5,6] *i.e.* to assume that guest molecules (dioxanes among them) get into the T-cavity[‡] under pressure. On the other hand, it is known that cyclohexane can form the CS-II hydrates only in the presence of an auxiliary component.[7]

Therefore, it was of interest to see whether THP – whose molecule is somewhat larger (7.14 A) than that of dioxane (7.03 A) but smaller than the cyclohexane molecule (7.38 A) – would form a CS-II hydrate at normal pressure or, moreover, a CS-I hydrate at elevated pressures.

Tetrahydropyran (THP) was obtained by the hydrogenation of dehydropyran, of which 180 ml was placed into an autoclave together with a Raney nickel catalyst. The hydrogen pressure was brought to 120 atm and maintained for 2 h at 100 °C. The reaction mixture was filtered off from the catalyst and the filtrate was treated with 10 ml of amyl alcohol with the addition of 0.5 g of *p*-toluenesulfonic acid (to remove the unreacted dehydropyran) and then distilled with a high dephlegmator. The purity control of the selected fractions was performed using a gas-liquid chromatography method (Chrom-42 chromatograph). The IR spectrum obtained in a thin 0.02 mm layer on a Specord M80 instrument coincided fully with the IR spectrum of THP in a thin 0.025 mm layer[8] recorded on a Shimadzu AR-275 IIS instrument.

To study the clathration process the differential thermal analysis (DTA) high pressure method was used as described in refs. 2 and 9. The mutual solubility of water and THP was studied by the Alekseyev polythermal method,[10] in which a mixture of water and THP of a known composition was sealed into a glass ampoule and then the temperature of appearance (disappearance) of turbidity, *i.e.* of a second liquid phase, was recorded.

Powder X-ray diffraction data on the $THP\cdot17H_2O$ hydrate (CS-II) was carried out using an automated diffractometer DRON-3M (CuKα, radiation, Si standard) at *ca.* −60 °C.

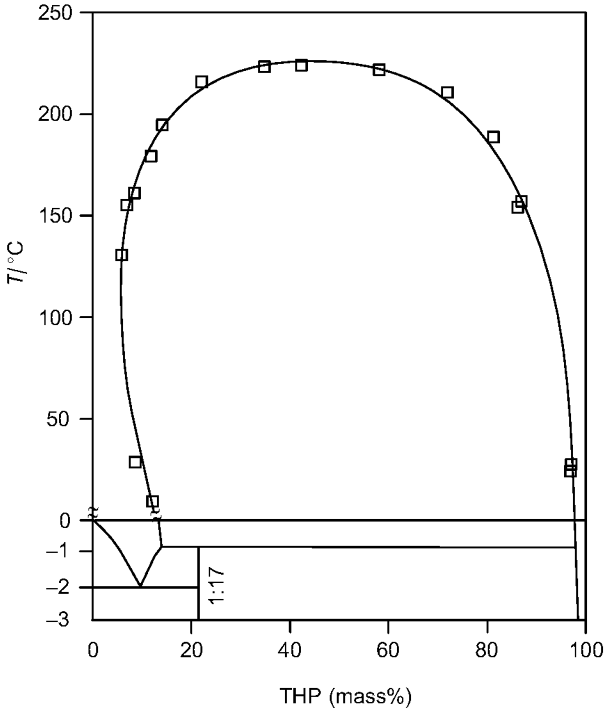

Fig. 1 Phase diagram for the H_2O–THP system at 1 atm in the clathrate formation and mutual solubility range.

Fig. 1 shows a phase diagram in the H_2O–THP system at 1 atm with a binodal which has an upper consolute temperature of dissolution equal to 226 °C at a concentration of *ca.* 47 mass%. Intersecting the crystallization range of the CS-II hydrate of composition $THP\cdot17H_2O$ (that the composition is such will be substantiated below) by the binodal produces at −0.8 °C a syntectic type of diagram. At low THP concentrations and temperatures 80–100 °C a retrograde solubility is observed (from 13.6% at −0.8 °C to *ca.* 6% by mass at 90 °C) which may be associated with the destruction of the clathrate-like structure of the solution upon heating.[11]

Fig. 2 shows the variation of the decomposition temperature with elevated pressure in the THP–H_2O system. The decomposition temperature of the CS-II hydrate decreases from $T = -0.8$ °C at normal pressure to −4.3 °C at $P = 1.15$ kbar (see Fig. 2, curve 1). Above this pressure a hydrate with a lower water content is formed. This can be judged by the appearance of considerable endothermal aqueous–eutectic melting effects for the CS-I hydrate, which is stabilized by pressure and which melts with decomposition into two liquids and at $P = 2.5$ kbar already reaches $T = 9.2$ °C (see Fig. 2, curve 2).

Such a picture is characteristic of systems forming CS-II hydrates under normal pressure in general[4] and (as mentioned previously) of systems with cyclic ethers in particular.[2]

If it is assumed that in this system (THP–H_2O), as in systems with THF and dioxanes,[2] there forms under normal pressure a CS-II hydrate in which only large cavities (H-cavities) are occupied then the filling of small dodecahedral (D-) cavities (the number of small D-cavities in the CS-II structure is twice that of the large H-cavities[4]) by auxiliary guest (X) molecules must produce a pressure-stabilized double hydrate of a composition $G\cdot2X\cdot17H_2O$. It is seen from Fig. 3 (curve 1) that in an excess of xenon with an increase in

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[†] The H-cavity is a 16-hedron ($5^{12}6^4$), which is a large cavity of CS-II.

[‡] The T-cavity is a 14-hedron ($5^{12}6^2$), which is a large cavity of CS-I.

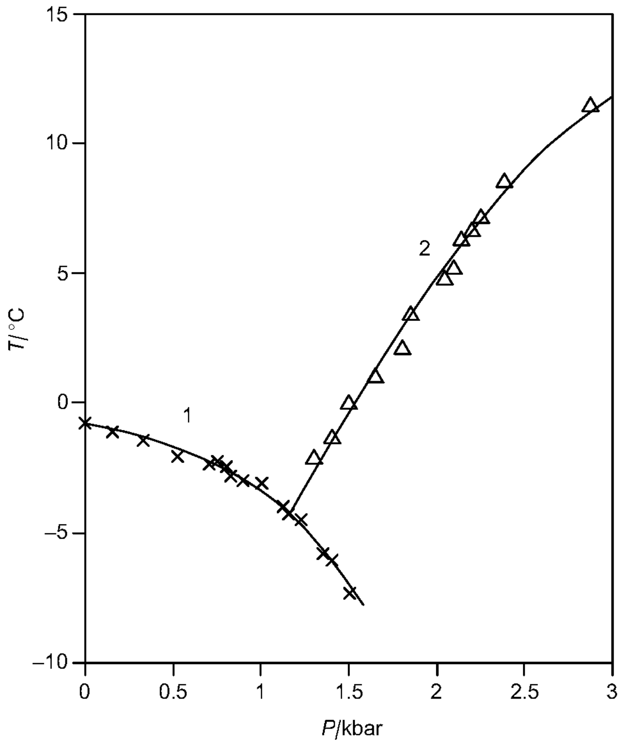

Fig. 2 Pressure dependence of the decomposition point of THP hydrates. 1, THP·$17H_2O$ and 2, THP·mH_2O ($m < 17$).

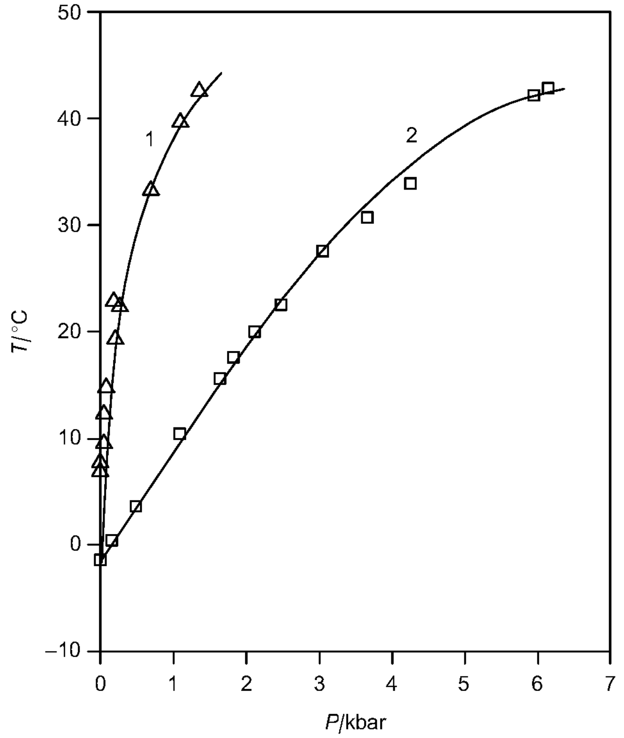

Fig. 3 Pressure dependence of the decomposition point of double hydrates. 1, THP·$2y$Xe·$17H_2O$ ($0 < y < 1$) and 2, THP·$0.5Pr_4NF·16H_2O$.

pressure ($dT/dP = 55.0$ K $kbar^{-1}$) there is a sharp increase in the decomposition temperature of the hydrate of composition THP·2Xe·$17H_2O$ with the initial structure (CS-II) and this remains over the whole range of pressures studied, as indicated by the absence of first-order phase transitions (*cf.* Fig. 2). An analoguous picture is observed for tetrapropylammonium fluoride as auxilary guest component (a double CS-II hydrate of composition THP·$0.5Pr_4NF·16H_2O$ is formed)[12] although the value of $dT/dP = 11.0$ K $kbar^{-1}$ is essentially smaller. In this case the tetrapropylammonium cation lies in the D_4-cavity which can only exist in a CS-II framework[§] since only this structure has a fragment with a tetrahedral (relative to the common vertex) arrangement of dodecahedral cavities. These experiments show indirectly that the hydrate under study is CS-II.

In direct measurements of the cell symmetry obtained by X-ray powder diffraction the cells are shown to be cubic with the parameter $a = 17.49$ A, and therefore the hydrate composition, as for all hydrates of this structure, must be 1:17.[4]

In the absence of an auxiliary guest hydrate this structure is destabilized by pressure (*i.e.* $dT/dP < 0$) due to the high concentration of vacant dodecahedral cavities and when these cavities are filled dT/dP is positive. It should be noted, however, that the double hydrate of THP with tetrapropylammonium fluoride (unlike that with xenon) under normal conditions melts at a temperature that is 0.6 °C lower than in the case of the simple hydrate. This results from a D_4-cavity being formed with breaking of four hydrogen bonds and a distortion of the framework. It is also the decreased water concentration of the equilibrium solution as a result of tetrapropylammonium dissolution in water (hydration of its ions) that leads to the decrease in melting temperature. However, since all these processes are little dependent on pressure (within the range of pressures under study), their effects are also only little changed with change in pressure. In contrast, the increase in the stabilizing effect (as a result of the filling of small cavities) with pressure is considerable and dT/dP is therefore positive. The filling of the vacant cavities in the CS-II framework, compaction of the hydrate, thus makes unnecessary a rearrangement of the framework and in the interval of pressure studied the double hydrates (unlike the simple CS-II hydrates) do not undergo any phase transitions.

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[§] The tetrapropylammonium cation occupies four adjacent D-cavities which have a tetrahedral arrangement and displace from the common vertex one water molecule with its central atom without the formation of an H-bond with the framework molecules. The fluoride ion, replacing a water molecule and forming H-bonds with neighbours, builds up together with them a water-anionic framework.[12]