

Cubic Structure II Double Clathrate Hydrates with Tetra(*n*-Propyl)Ammonium Fluoride*

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Abstract. A double clathrate hydrate with the composition $\text{THF} \cdot 0.5(n\text{-Pr})_4\text{NF} \cdot 16 \text{H}_2\text{O}$ and cubic structure II (CS-II, $a = 17.67 \text{ \AA}$) has been obtained. Its experimental density is $1.053 \pm 0.001 \text{ g/cm}^3$; its melting point is 8.1°C , i.e. 3.1°C higher than that of the $\text{THF} \cdot 17 \text{H}_2\text{O}$ hydrate. The double hydrates of acetone, 1,4-dioxan, trimethyleneoxide and 1,3-dioxolane with $(n\text{-Pr})_4\text{NF}$ have melting points of -14.8 , -5.5 , -2.6 and -9.6°C , respectively. With pressure increase up to 6 kbar the melting points of the double hydrates increase monotonously in contrast to common CS-II hydrates. The friability of the structure of the hydrates (the packing coefficient) and their sensitivity to pressure (dT/dP) are compared.

Key words. Double clathrate hydrate, high pressure, packing coefficient, tetra(*n*-propyl)ammonium fluoride.

1. Introduction

Jeffrey has shown that the gas hydrates and the clathrate hydrates of peralkylonium salts are closely related [1, 2] and exist in a variety of framework structures [3, 4]. Cubic structure II (CS-II), which is very common for gas hydrates, is the only structure which has not been prepared in the case of hydrates of peralkylonium salts, though such attempts have been undertaken [2]. Jeffrey attributed this to the unfavourable arrangement of large and small cavities. We note that the small cavities in CS-II are arranged tetrahedrally, and on the assumption that the size of the *n*-propyl group fits¹ the dodecahedral cavity well we envisage that $(n\text{-Pr})_4\text{N}^+$ can be situated in a 4-section D_4 -cavity.² In addition, we know [5, 6] that in the concentration range concerned $(n\text{-Pr})_4\text{N}^+$ by itself does not form a clathrate since, with all big cavities empty, the filling of only small cavities by $(n\text{-Pr})_4\text{N}^+$ is not sufficient to stabilize CS-II. This is why $(n\text{-Pr})_4\text{N}^+$ could be expected to participate in clathrate formation as an auxiliary component.

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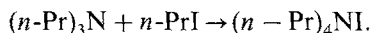
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¹ Not only the comparison of its Van der Waals dimensions with the size of the cavity, but also experiments on the inclusion of the hydrophobic part of carboxylate anions [7, 8] show that the *n*-propyl group fits excellently into the *D*-cavity.

² This is true if one assumes the manner of the cation arrangement to be the same as in the familiar peralkylonium salt hydrates, i.e. the central cation atom is situated in a vertex shared by four polyhedra. The radicals are situated in the sections of the D_4 -cavity, and the anion is included into the framework in a hydrophilic way.

2. Experimental

The substances used in the experiment were twice distilled tetrahydrofuran (THF), trimethyleneoxide (TMO), 1,4-dioxan (1,4-D), acetone (Ac), 1,3-dioxolane and water. $(n\text{-Pr})_4\text{NI}$ was synthesized by the reaction:



After that the initial tetra(*n*-propyl)ammonium fluoride–water solution was prepared by an ion exchange reaction with AgF. Its concentration was determined as described later. All the solutions used were prepared from the initial solution and water by weighing. The water content was determined by the Karl Fischer technique with an error of 0.6%; the $(n\text{-Pr})_4\text{NF}$ content was determined by titration with sodium tetraphenylborate in the presence of a cation selective electrode [9] (error 0.5%). All the experiments were carried out in a helium atmosphere to exclude filling of the *D*-cavities by molecules of atmospheric gases. The double THF hydrate crystal density was determined by the flotation technique at 0°C in mixed cyclohexane–CCl₄–THF solutions. The latter was added to the solution to prevent washing THF out of the crystal. The isolation of the double THF hydrate crystals for chemical analysis, the determination of the density and the X-ray study were carried out at 0°C in air, which was in equilibrium with 20% THF water solution. The recording of the X-ray diffraction spectrum was carried out using an automated diffractometer (CuK_α radiation, Si standard) at about –60°C.

3. Results and Discussion

3.1. INVESTIGATIONS AT ATMOSPHERIC PRESSURE

If cation and anion inclusion is hydrophobic–hydrophilic and the cavities are fully occupied, the composition of a double THF hydrate should be THF·0.5(*n*-Pr)₄NF·16 H₂O. Hence the hydrate was crystallized from a solution with the composition close to that assumed for the double hydrate.

Table I shows the results of the double hydrate THF and $(n\text{-Pr})_4\text{NF}$ analysis (9 samples). $(n\text{-Pr})_4\text{NF}$ and THF were used in excess because the formation of solid solutions is possible (though this is not so obvious as in the case where an auxiliary component is a gas, when its molecule occupies the available *D*-cavity), and we sought

Table I. The results of the analysis of the double THF and $(n\text{-Pr})_4\text{NF}$ hydrate crystals obtained (9 independent measurements).

| Substance | Calculated according to formula THF·0.5(<i>n</i> -Pr) ₄ NF·16 H ₂ O (weight %) | Analysis of crystals (weight %) | Error of the average | Stoichiometry* | Error for 95% confidence |
|----------------------------|---|---------------------------------|----------------------|----------------|--------------------------|
| H ₂ O | 62.25 | 62.81 | 0.29 | 16.0 | 0.17 |
| $(n\text{-Pr})_4\text{NF}$ | 22.18 | 22.05 | 0.18 | 0.493 | 0.009 |
| THF | 15.57 | 15.14** | 0.34 | 0.964 | 0.051 |

* Calculated for 16 water molecules.

** On the basis of the difference.

to prepare a hydrate with a composition close to the maximum content of $(n\text{-Pr})_4\text{NF}$. The excess THF was also necessary to compensate for possible THF losses due to evaporation.

The results of Table I together with the X-ray data (cubic structure, $a = 17.67 \text{ \AA}$) suggest that the double hydrate obtained really belongs to cubic structure II with the cavities fully occupied by both guests. The experimental density of the double hydrate is $1.053 \pm 0.001 \text{ g/cm}^3$. The volume of the cell increases appreciably relative to that of the $\text{THF} \cdot 17 \text{ H}_2\text{O}$ hydrate ($a = 17.18 \text{ \AA}$ [10]) and those of all the CS-II hydrates. Such an increase of the cell volume is observed for CS-I (or its superstructure with doubled a parameter) with the transition from gas hydrates ($a = 12.05 \pm 0.1 \text{ \AA}$) [10] to the hydrates of peralkylonium salts ($a = 12.3 \pm 0.1 \text{ \AA}$) [4]. This seems to be due to framework distortion, occurring during the formation of a 4-section cavity, whereby the central cationic N atom replacing a water molecule forces the adjacent water molecules apart to a distance of $\sim 4.0 \text{ \AA}$ instead of 2.8 \AA , as is the case with the idealized framework [1, 2]. These distortions seem to make the increase of the thermal stability in the case of the double $\text{THF} \cdot 0.5(n\text{-Pr})_4\text{NF} \cdot 16 \text{ H}_2\text{O}$ hydrate much less (m.p. = 8.1°C) as compared to the double $\text{THF} \cdot \text{H}_2\text{S} \cdot 17 \text{ H}_2\text{O}$ hydrate (m.p. = 21.3°C) [16].

Similar results are provided by a study of the mixtures with the composition of the double Ac, 1,4-D and TMO hydrates. Table II shows the results of comparing the melting points of these hydrates with those of simple³ CS-II hydrates. In the case of 1,4-D, Ac or TMO the melting point is seen to increase. In the case of 1,3-dioxolane the melting point of the mixture with the composition of the corresponding double hydrate is observed to decrease considerably. The absence of any effects in the thermogram in the range of -60 to -15°C is indicative of the formation of a double hydrate (Figure 1). In addition, the mixture melting point increases with pressure, which would be impossible if the simple 1,3-dioxolane hydrate or ice were crystallized (Figures 2, 5). One can hardly explain this only by framework distortion during hydrophobic-hydrophilic inclusion of $(n\text{-Pr})_4\text{NF}$, though distortion does occur [1] if it is included in the same way as a tetra(*n*-butyl)ammonium cation. This is supported by the fact that the stabilization by $(n\text{-Pr})_4\text{NF}$ is appreciably weaker than the stabilization by hydrogen sulphide which is generally used as an auxiliary component. The melting point of the $\text{Ac} \cdot 2 \text{ H}_2\text{S} \cdot 17 \text{ H}_2\text{O}$ hydrate is 8.9°C [16]. Figure 1 shows that the mode of melting of the double 1,4-D, Ac and TMO hydrates

Table II. The change of the melting point of the double hydrates with $(n\text{-Pr})_4\text{NF}$ relative to that of simple hydrates with the composition 1 : 17.

| Main guest | m.p. of hydrate 1 : 17, $^\circ\text{C}$ | m.p. of double hydrate with $(n\text{-Pr})_4\text{NF}$, $^\circ\text{C}$ | Δ m.p., $^\circ\text{C}$ |
|---------------|--|---|---------------------------------|
| TMO | -9.2 [14] | -2.6 | 6.6 |
| Acetone | -20.0 [9] | -14.8 | 5.2 |
| 1,4-D | -9.1 [11] | -5.5 | 3.7 |
| THF | 5.1 [35] | 8.1 | 3.0 |
| 1,3-dioxolane | -1.5 [12] | -9.6 | -8.1 |

³ The simple hydrate is a single-guest hydrate.

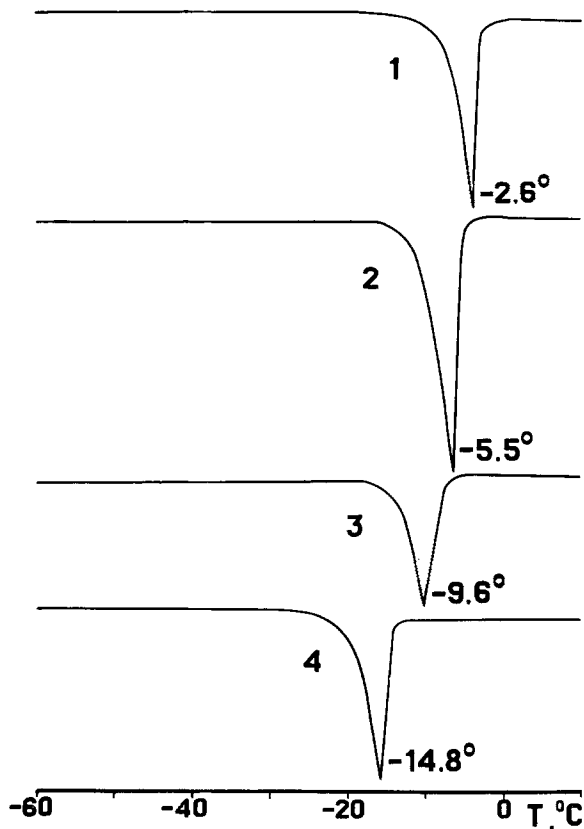


Fig. 1. DTA curves of melting of the mixtures with the composition of double TMO (1), 1,4-D (2), 1,3-dioxolane (3) and Ac (4) hydrates with $(n\text{-Pr})_4\text{NF}$. Temperature versus time curves are not depicted for simplicity.

also changes. Simple hydrates melt incongruently whereas the double TMO and 1,4-D hydrates melt congruently, which is indicated by the values of the melting points themselves. As for the acetone double hydrate, with a rather low melting point, it may melt incongruently, but the composition of the peritectic point is similar to that of the hydrate, and within experimental error it is impossible to distinguish between the effects of peritectic melting and those of ice melting. The absence of endothermic effects on the heating curves, except for the melting effect, in all these cases (Figure 1) shows that the hydrates melt congruently and the composition of the initial solutions agrees closely with that of the hydrate.

3.2. INVESTIGATIONS AT HIGH PRESSURES

Very useful information on clathrate formation in aqueous systems is provided by investigations at high pressure, especially in regard to the formation of CS-II hydrates. Such investigations have the following advantages.

1. Ice I_h , as a host component, possesses a rare ability to be destabilized by pressure (Table V), i.e. pressure facilitates the destruction of the ice crystalline structure.

- The packing coefficient⁴ of clathrate hydrates is larger than that of ice (Figure 5, Table V). Therefore they are generally stabilized by pressure. Even in the rare instance of destabilization (as is the case with CS-II hydrates), it occurs to a lesser degree than in ice itself.
- Water can form clathrate hydrates of various structures. Because their packing coefficients vary widely, pressure has various effects on them.

Of all the clathrate hydrates the most interesting from the point of view of pressure effects are CS-II hydrates since the ratio of the quantities of the small to big cavities is the largest (Table III). Thorough analysis carried out by Davidson revealed that in CS-II hydrates with large guest molecules (composition 1:17) the degree of filling of the cavities does not differ significantly from 1 [10]. However, such molecules do not fill the small cavities at all.⁵ In this case a very friable structure is formed, and the hydrates of this structure are destabilized by pressure [3, 4]. Another effect should be observed if the small cavities are filled, since in this case the packing coefficient should increase significantly. As we have already mentioned, even under ordinary conditions the stability increases at the expense of the packing efficiency. However, a still greater effect may be expected when pressure is exerted.

Figure 2 shows the melting points of simple THF hydrates and a double THF·0.5(*n*-Pr)₄NF·16 H₂O hydrate. The picture is seen to differ radically. While the THF·17 H₂O hydrate is destabilized by pressure, to give firstly the hydrate THF·7 H₂O and then the THF·5 H₂O hydrate, the melting point of the THF·0.5(*n*-Pr)₄NF·16 H₂O hydrate increases monotonously from 8.1°C at 1 atm to 42.8°C at 6.2 kbar, which means that no other hydrates are formed in this pressure range. This is what should be expected because the packing coefficient of this double hydrate is very large in comparison with that of other hydrates (Table V). For comparison Figure 2 depicts the melting curve of ices under pressure. The ices were obtained from (*n*-Pr)₄NF solution with the composition 1:32, i.e. like that of a double hydrate. The ice melting point in such a solution is in agreement with the data of [6]. With the pressure increase the melting curve goes down,

Table III. The ratio of small and big cavities in the structures of some clathrate hydrates [4].

| Structure type | Unit cell content | Ratio of numbers of small and large cavities |
|----------------|---------------------------------------|--|
| CS-I | 6 T·2 D·46 H ₂ O | 0.33 |
| Tetragonal I | 4 P·16 T·10·D·172 H ₂ O | 0.50 |
| Hexagonal I | 2 P·2 T·3 D·40 H ₂ O | 0.75 |
| Rhombic | 4 H·4 P·4 T·14 D·148 H ₂ O | 1.17 |
| CS-II | 8 H·16 D·136 H ₂ O | 2.00 |

⁴ k is the packing coefficient equal to $\Sigma v_i/V$, where Σv_i is the total volume of the molecule, forming the phase with the volume V [17].

⁵ In recent papers Davidson and coworkers have shown that sufficiently small species, such as Ar, Kr, O₂, N₂ [18, 19] also stabilize CS-II rather than CS-I, whose stabilization would seem to be more likely because of the smaller difference in the dimensions of the big and small cavities. Due to filling of the small cavities, it is the CS-II hydrate that is stabilized, which we refer to as self-stabilization.

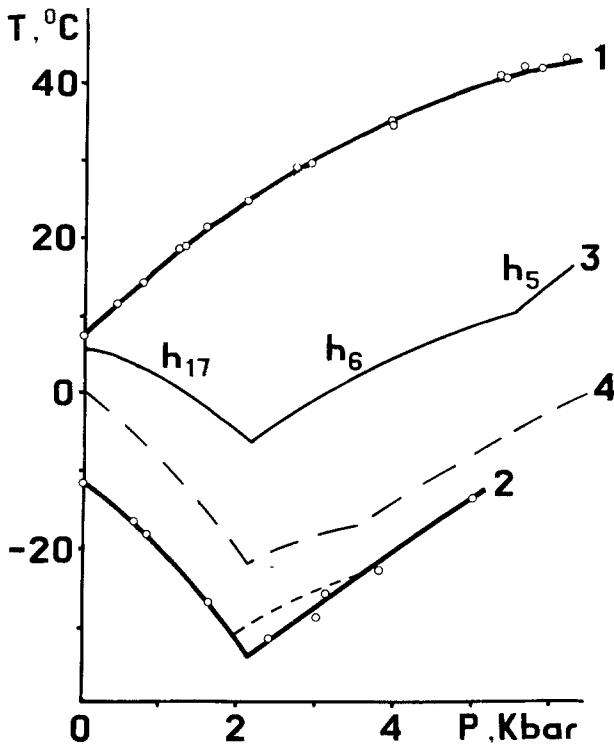


Fig. 2. Melting point dependence upon pressure. (1) of the double THF·0.5 (*n*-Pr)₄NF·16 H₂O hydrate; (2) of ice mixed with (*n*-Pr)₄NF (the ratio of the components (*n*-Pr)₄NF : H₂O = 1 : 32 is the same as that of the double THF·0.5(*n*-Pr)₄NF·16 H₂O hydrate); (3) of THF hydrates for the mixtures containing THF and water in the ratio 1 : 17, *h*₁₇ = THF·17 H₂O, *h*₆ = THF·6 H₂O, *h*₅ = THF·5 H₂O; (4) of ices under pressure. Curve 2 is seen to represent the melting of ices I and V in (*n*-Pr)₄NF solution. We have not managed to obtain the stable part of the ice III curve.

then it breaks at ~2.1 kbar and goes upwards. The slopes of these curves are seen to be similar to those of ices Ih and V. Ice III, stable in the pressure range 2.1–3.6 kbar, has not been detected because of the kinetics of its formation. No detailed experiments have been carried out in this field.

A similar behaviour under pressure is observed for the double hydrates of 1,4-D, Ac, TMO and 1,3-dioxolane with (*n*-Pr)₄NF (Figures 3, 4). Note that the stabilization of hydrates correlates qualitatively with the molecular volume of the main guest⁶ (Table IV).

The first attempt to correlate the degree of friability of these hydrates with their stability under pressure has been made in [20]. In the present paper we will try to determine the semiquantitative relation between the degree of friability of the structure, characterized as the packing coefficient, and its liability to the pressure effects, referred to as dT/dP for melting (χ) at 1 atm. Figure 5 and Table V illustrate the dependence of χ upon $1/k$. If one assumes that during melting the molecular volume does not change

⁶ The main guest is the guest occupying the big cavities.

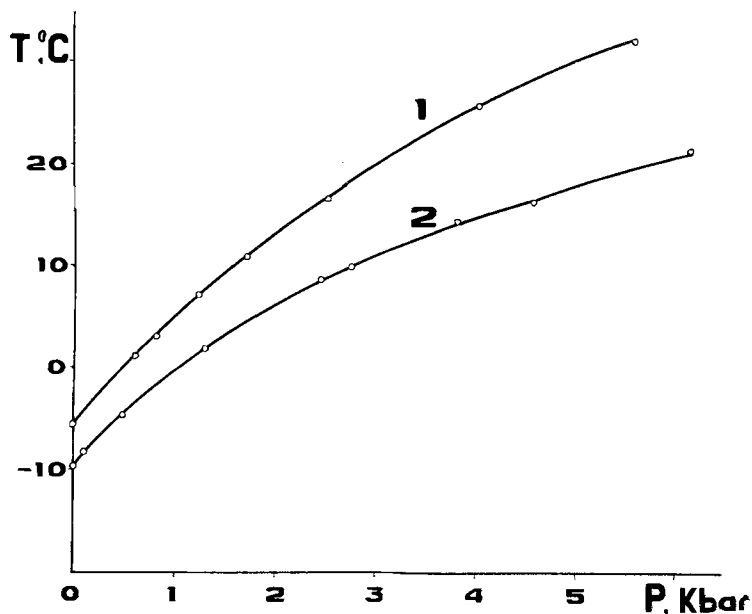


Fig. 3. The dependence of the mixtures with the composition of the double 1,4-D (1) and 1,3-dioxolane (2) hydrates with $(n\text{-Pr})_4\text{NF}$ upon pressure.

appreciably, then the Clausius-Clapeyron equation can be written in terms of k as follows:

$$\chi = \frac{\sum v_i}{\Delta S_{\text{melt}}} \left(\frac{1}{k_l} - \frac{1}{k_s} \right) = T_{\text{melt}} \cdot \frac{\sum v_i}{\Delta H_{\text{melt}}} \left(\frac{1}{k_l} - \frac{1}{k_s} \right)$$

The approximate linear dependence of χ upon $1/k$ testifies to the fact that the ratio $\sum v_i / \Delta S_{\text{melt}}$ and the changing of the liquid phase packing from system to system are negligible, and it is the changing of the solid phase packing coefficient which is determinant. The interrelation between the χ and $1/k$ values of the double hydrate, as one can see in Figure 5, is not an exception from the semi-quantitative dependence discussed above.

Table IV. dT/dP for melting of the double hydrates with $(n\text{-Pr})_4\text{NF}$ at 1 atm and the volume of the main guest molecules.

| Main guest | Volume* of the guest molecule, Å ³ | dT/dP , K/kbar |
|---------------|---|------------------|
| 1,4-D | 79.7 | 12.0 |
| THF | 73.2 | 10.0 |
| 1,3-dioxolane | 63.7 | 10.4 |
| Acetone | 62.0 | 9.5 |
| TMO | 58.2 | 8.8 |

* The volumes of the molecules were calculated as in [17] using the values of Van der Waals radii cited in Table V and reference book values for the bond length and angles.

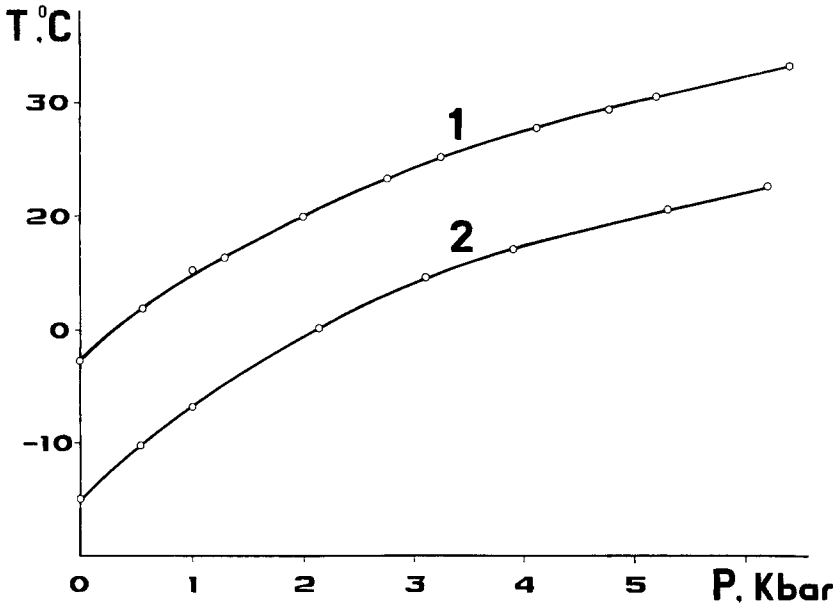


Fig. 4. The dependence of the mixtures with the composition of the double TMO (1) and Ac (2) hydrates with $(n\text{-Pr})_4\text{NF}$ upon pressure.

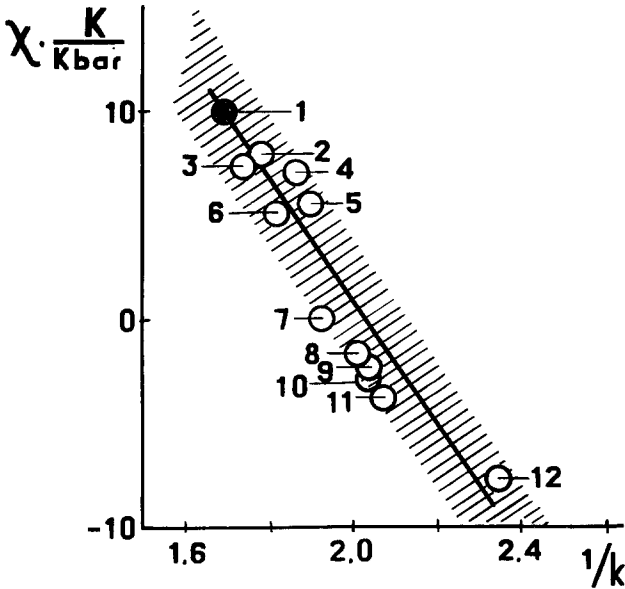


Fig. 5. The dependence of the velocity of the melting point change upon pressure (at 1 atm) (χ), relative to the inverse value of the packing coefficient (k). Figures indicate the correspondence between these points and the points of Table V.

Table V. The structure of clathrate hydrates and their stability to pressure.

| No. | Guest component | Values used in calculations | | Guest ^a molecule volume, Å ³ | k | z: K/kbar at 1 atm |
|-----|--|-----------------------------|--|--|-------|------------------------|
| | | Hydrate number | System, cell parameters, Å | | | |
| 1. | THF + 0.5(n-Pr) ₄ NF | 16.0 | CS-II, a = 17.67 | 73.2 (THF) 217.3 (n-Pr) ₄ NF | 0.591 | 10.0 |
| 2. | (C ₂ H ₅) ₂ NH | 8.67 [21] | orthorhombic a = 13.44, b = 11.77 c = 27.91 [21] | 85.1 | 0.564 | 8.0 [4] |
| 3. | (n-C ₄ H ₉) ₄ NF | 28.6 [22] | super CS-I, a = 24.42 [23] | 294 | 0.576 | 7.2 ^b |
| 4. | C ₂ H ₄ O (ethylene epoxide) | 6.89 [10] | CS-I, a = 12.03 [10] | 42.7 | 0.537 | 7.0 [20] |
| 5. | SO ₂ | 6.0 [10] | CS-I, a = 11.97 [10] | 33.4 | 0.528 | 5.56 [24] |
| 6. | (n-C ₄ H ₉) ₄ NHCOO | 31.6 [25] | tetragonal I, a = 23.5, c = 12.4 [25] | 312 | 0.554 | 5.0 ^c |
| 7. | iso-C ₅ H ₁₁ (n-C ₄ H ₉) ₃ NBr | 38.0 [26] | orthorhombic, a = 12.1 ^d b = 21.6, c = 12.8 [27] | 331 | 0.519 | 0.0 [26] |
| 8. | CHCl ₃ | 17.0 [10] | CS-II, a = 17.33 [10] | 83.9 | 0.498 | -1.7 [28] |
| 9. | C ₄ H ₈ O (THF) | 17.0 [10] | CS-II, a = 17.18 [10] | 73.2 | 0.494 | -2.3 [29] -2.5 [30] |
| 10. | 1,3-dioxan | 17.0 [31] | CS-II, a = 17.28 ^e [32] | 79.7 | 0.496 | -3.0 [31] |
| 11. | 1,3-dioxolane | 17.0 [12] | CS-II, a = 17.12 [15] | 63.7 | 0.484 | -3.8 [12] |
| 12. | H ₂ O (ice Ih) | | density ρ = 0.9168 g/cm ³ | 14.1 ^f | 0.433 | -7.66 ^g |

^a The volumes were calculated using the following Van der Waals radii: R_C = 1.71 Å, R_H = 1.17 Å, R_O = 1.30 Å, R_N = 1.50 Å, R_S = 1.84 Å, R_{Cl} = 1.90 Å, R_{Br} = 1.96 Å, the length of an H-bond in a water framework is 2.80 Å.

^b From Yu. M. Zelenin (unpublished results).

^c From F. V. Zhurko and T. V. Mikina (unpublished results).

^d The parameters used are those of (iso-Am)₄NF·38 H₂O hydrate.

^e The parameters used are those of 1,4-D hydrate.

^f The same molecular volume was used in calculating packing coefficients of clathrate hydrates.

^g Calculated on the basis of the value of ΔV_{meit} = -1.632 cm³/mol, ΔH_{meit} = 6.012 kJ/mol according to the Clausius-Clapeyron equation.

Thus, it can be concluded that $(n\text{-Pr})_4\text{NF}$ that does not form clathrate hydrates [6] either at one atmosphere or at elevated pressures (for curve 2 see Figure 2) but it can provide additional stabilization of CS-II hydrates, when it is situated in the D_4 -cavity [4]. We should like to emphasize that for framework stabilization in CS-II it is enough to fill only the 8 big cavities with molecules of a suitable size with the 16 small cavities remaining vacant, but it is not enough to fill the 16 small cavities without also filling the big ones. However, the total free volume of the big cavities in a cell (1530 \AA^3) is even smaller than that of the small ones (1560 \AA^3). Therefore, the big cavities are the 'Achilles heel' of the framework structure, which is quite evident. It is appropriate here to see whether the classical Van der Waals approach is applicable to the description of hydrate systems. Can clathrate frameworks be considered to be metastable ice forms as the theory suggests? Or, are these frameworks absolutely unstable (labile)? Experimental evidence of their lability is presented in [33]. In the present paper we shall present some simple considerations. It is apparent that under ordinary conditions any crystalline structure built of water molecules is less stable than ice *Ih*. Therefore any structure will melt below 0°C . It is also known that a solid body can be overheated in a very narrow temperature range. This means that ice *Ih* cannot be obtained in a metastable state at temperatures even slightly above 0°C . Thus, at 0°C (the temperature at which the Van der Waals theory is generally applied) any clathrate framework can be considered labile. On the basis of stoichiometric data available now one cannot definitely say whether the framework is labile or metastable. Anyway as the experimental accuracy increases the experimental degree of filling of the big cavities can be seen to approach 1 [4, 34].

In CS-II hydrates with small guests (such as Ar, Kr, O_2 , N_2) [19, 20] due to self-stabilization through the filling of the small cavities, the degree of filling of the big cavities might be expected to differ from 1 more significantly. This difference could be experimentally detectable, but such data are not yet available.

In conclusion one can say that $(n\text{-Pr})_4\text{NF}$ is an auxiliary component in the formation of double CS-II hydrates. However, one can expect that $(n\text{-Pr})_4\text{NF}$ is a less universal component as compared to H_2S , Ar, Xe etc., since its inclusion requires the presence of a multisectional D_4 -cavity.

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References

1. G. A. Jeffrey and R. K. McMullan: *Prog. Inorg. Chem.* **8**, 43 (1967).
2. G. A. Jeffrey: *Hydrate Inclusion Compounds (Inclusion Compounds v. 1*, Ed. J. L. Atwood, J. E. D. Davies and D. D. MacNicol), pp. 135–182, Academic Press, London (1984).
3. Yu. A. Dyadin and K. A. Udachin: *J. Incl. Phenom.* **2**, 61 (1984).
4. Yu. A. Dyadin and K. A. Udachin: *Zh. Strukt. Khim.* **28**, 75 (1987).
5. Fowler D. L., W. A. Loebenstein, D. B. Pall, C. A. Kraus: *J. Am. Chem. Soc.* **62**, 5, 1140 (1940).
6. H. Nakayama and K. Watanabe: *Bull. Chem. Soc. Jpn.* **49**, 1254, (1976).
7. Yu. A. Dyadin, L. A. Gaponenko, and L. S. Aladko: *Izv. Sib. Otd. Akad. Nauk SSSR. Ser. Khim. Nauk* **60** (1986).
8. Yu. A. Dyadin, L. A. Gaponenko, L. S. Aladko, and S. V. Bogatryyova: *J. Incl. Phenom.* **2**, 259 (1984).
9. B. S. Smolyakov, Yu. A. Dyadin, and L. S. Aladko: *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk* **66** (1980).

10. D. W. Davidson: in *Water. A Comprehensive Treatise*. v. 2. Water Crystalline Hydrates. Aqueous Solutions of Simple Nonelectrolytes, p. 115, New York, London (1973).
11. Yu. A. Dyadin, I. V. Bondaryuk, G. L. Rijikova, E. Ya. Aladko, and Yu. M. Zelenin: *Izv. Sib. Otd. Akad. Nauk SSSR*, Ser. Khim. Nauk 67 (1984).
12. Yu. A. Dyadin, P. N. Kuznetsov, and I. I. Yakovlev: *Izv. Sib. Otd. Akad. Nauk SSSR*, Ser. Khim. Nauk 30 (1976); *Chem. Abstr.* **84**, 156307a (1976).
13. Yu. A. Dyadin, Yu. M. Zelenin, S. G. Bezuglov, and I. V. Bondaryuk: *Izv. Sib. Otd. Akad. Nauk SSSR*, Ser. Khim. Nauk 70 (1978); *Chem. Abstr.* **89**, 169844b (1978).
14. R. E. Hawkins and D. W. Davidson: *J. Phys. Chem.* **70**, 1889 (1966).
15. F. D. Sargent and L. Colvert: *J. Phys. Chem.* **70**, 2689 (1966).
16. D. N. Glew, H. D. Mak and N. S. Rath: *Hydrogen-Bonded Solvent Systems*, London, Taylor and Francis, p. 195 (1968).
17. A. I. Kitaygorodskii: *Molekulyarnie Kristalli*, Moskva, Nauka, p. 27 (1971).
18. D. W. Davidson, S. R. Gough, Y. P. Handa, C. I. Ratcliffe, J. A. Ripmesster, and J. S. Tse: 4-th Intern. Symp. on Inclusion Phenomena, Abstracts, Lancaster, p. 72 (1986).
19. D. W. Davidson and Y. P. Handa: *Nature* **311**, 142 (1984).
20. Yu. A. Dyadin, P. N. Kuznetsov, and I. I. Yakovlev: *Izv. Sib. Otd. Akad. Nauk SSSR*, Ser. Khim. Nauk 72 (1975); *Chem. Abstr.* **83**, 183516b (1975).
21. R. K. McMullan, T. H. Jordan, and G. A. Jeffrey: *J. Chem. Phys.* **47**, 1218 (1987).
22. Yu. A. Dyadin, I. S. Terekhova, T. M. Polyanskaya, and L. S. Aladko: *Zh. Strukt. Khim.* **17**, 655 (1976).
23. Yu. A. Dyadin, P. N. Kuznetsov, and I. I. Yakovlev: *Dokl. Akad. Nauk SSSR* **203**, 825 (1972).
24. J. G. Van Berkum and G. A. M. Diepen: *J. Chem. Thermodyn.* **11**, 317 (1979).
25. Yu. A. Dyadin, L. S. Aladko, and L. A. Gaponenko: *Izv. Sib. Otd. Akad. Nauk SSSR*, Ser. Khim. Nauk 19 (1981); *Chem. Abstr.* **95**, 176581r (1981).
26. P. N. Kuznetsov, Yu. A. Dyadin, and I. I. Yakovlev: *Izv. Sib. Otd. Akad. Nauk SSSR*, Ser. Khim. Nauk 30 (1984); *Chem. Abstr.* **81**, 96833v (1974).
27. D. Feil and G. A. Jeffrey: *J. Chem. Phys.* **35**, 1863 (1961).
28. G. Tamman and G. J. Kriege: *Z. Anorg. Allg. Chem.* **146**, 191 (1925).
29. D. W. Davidson, S. K. Garg, S. R. Gough, Y. P. Handa, C. I. Ratcliffe, J. S. Tse and J. A. Ripmeester: *J. Incl. Phenom.* **2**, 231 (1984).
30. Yu. A. Dyadin, P. N. Kuznetsov, and I. I. Yakovlev: *Izv. Sib. Otd. Akad. Nauk SSSR*, Ser. Khim. Nauk 2, 3 (1972); *Chem. Abstr.* **77**, 156607d (1972).
31. Yu. M. Zelenin, Yu. A. Dyadin, and F. V. Zhurko: *Viniti* 5239 (1984).
32. S. R. Gough, J. A. Ripmeester, and D. W. Davidson: *Can. J. Chem.* **53**, 2215 (1975).
33. Yu. A. Dyadin and V. R. Belosludov: *Izv. Sib. Otd. Akad. Nauk SSSR*, Ser. Khim. Nauk 72 (1986).
34. D. W. Davidson, Y. P. Handa, and J. A. Ripmeester: *J. Phys. Chem.* **90**, 6549 (1986).
35. Yu. A. Dyadin, P. N. Kuznetsov, I. I. Yakovlev and A. V. Pyrinova: *Dokl. Akad. Nauk SSSR* **208**, 103 (1973); *Chem. Abstr.* 102558r (1973).