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Double Clathrate Hydrate in the $(CH_3)_4NF$-$(C_3H_7)_4NF$-H_2O System

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Clathrate formation in the system $(CH_3)_4NF$-$(C_3H_7)_4NF$-H_2O was studied using the differential thermal analysis technique. The double clathrate hydrate $(CH_3)_4NF$. $0.5(C_3H_7)_4NF{\cdot}15H_2O$ melting congruently at 21.7 °C was found in the system. The hydrate forms a hexagonal cell with a = 12.290(5), c = 59.35(1) Å; D = 1.091 g·cm^{-3}, and the packing coefficient is 0.603. Pressure increase causes the stabilization of the double hydrate.

INTRODUCTION

Double clathrate hydrates form when the main guest molecules occupy the large cavities (T, P, H, E[1]), while the additional component molecules are accommodated in the small D-cavities[1] (pentagonal dodecahedra) or the D′-cavities $4^3 5^6 6^3$[‡] (in the case of the hexagonal structure H[2]). Each molecule of the additional component can either occupy only one small cavity, as is the case with H_2S, O_2, N_2, Xe, and other suitable molecules[3], or, like the Pp_4N^+ cation (Pp stands for C_3H_7), be arranged in the 4-section D_4-cavity[4], forcing out the water molecule shared by all four D-cavities. The framework in this kind of hydrates can consist of water only, as in the $THF{\cdot}2H_2S{\cdot}17H_2O$ hydrate[5], or water and anions, as in the $THF{\cdot}0.5Pp_4NF{\cdot}16H_2O$ hydrate[4].

In all the systems studied earlier the guest used as the main component was able to form the common cubic structure II (CS-II) hydrates even in the absence of Pp_4NF (e.g. THF, 1,4-dioxane, thrimethyleneoxide (TMO), etc). The object of this work was to learn if clathrate formation is possible when Me_4N^+ (Me stands for CH_3), which is not capable of forming CS-II clathrate hydrates without an additional guest, is used. It is known that the cation Me_4N^+ can occupy one of the large cavities (P-cavities[1]) to give the hydrate $Me_4NOH{\cdot}7.5H_2O$ (β-form)[6]. The P-cavity ($5^{12}6^3$) is of somewhat extended shape and is a little smaller in comparison with the H-cavity $5^{12}6^4$. The smallest free diameter of the P-cavity is 6.1 Å, and that of the H-cavity, 6.6 Å. From the point of view of symmetry the H-cavity is more beneficial for the Me_4N^+ cation than the P-cavity. However, it turns out that the

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filling of the large P-cavities by the cations Me_4N^+ will suffice for the stabilization of tetragonal structure II (TS-II) even if all the decahedral cavities 4^25^8 remain vacant (the ratio of the large to small cavities in TS-II is 2). However, to stabilize the structure CS-II it is not enough to fill the large H-cavities with the cations Me_4N^+ but to leave many pentagonal dodecahedra vacant (the ratio of the large to small cavities in CS-II is 0.5). The cation Me_4N^+ does not seem to stabilize the large H-cavity well enough and does not form the hydrate $Me_4NOH{\cdot}16H_2O$[6] with vacant D-cavities. However, it was expected that the use of Pp_4NF as an additional component might make the formation of the double clathrate hydrate with the cation Me_4N^+ in 16-hedral H-cavity possible. It would be the first case of the formation of the double hydrate with tetraalkylammonium salts as both the main and an auxiliary guest.

RESULTS AND DISCUSSION

Nine sections of the tertiary $Me_4NF - Pp_4NF - H_2O$ system (Fig. 1) have been studied. In the system a congruently melting compound $Me_4NF{\cdot}0.5Pp_4NF{\cdot}15H_2O$ forms (Fig. 2), whose composition is consistent with the assumed structure. The stoichiometry of the double clathrate suggests that the whole of the Me_4N^+ cation is situated in one large H-cavity, and the Pp_4N^+ cation is situated in a 4-section D_4-cavity, while the nitrogen atom takes the place of the water framework oxygen atom common for four D-cavities (Fig. 3). Fluoride ions displace the water molecules in the framework, forming a water-fluoride framework.

The analysis of the double hydrate crystals grown from aqueous solutions gives the following composition: $1.008(8)Me_4NF{\cdot}0.498(4)Pp_4NF{\cdot}14.97(9)H_2O$. The determination errors for 95% confidence and for 5 independent measurements are given in brackets. The experimental composition is close to the expected one, $Me_4NF{\cdot}0.5Pp_4NF{\cdot}15H_2O$.

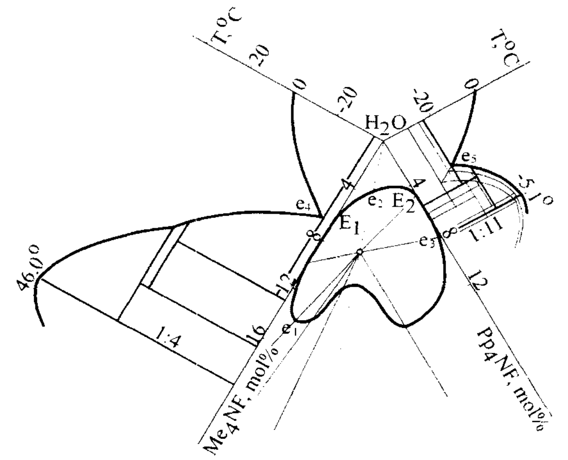

FIGURE 1 Phase diagram projection of the $Me_4NF - Pp_4NF - H_2O$ system in the field of clathrate formation.

The double system $Pp_4NF - H_2O$ was studied earlier by us[7]. The sections $Me_4NF{\cdot}4H_2O - Me_4NF{\cdot}0.5Pp_4NF{\cdot}15H_2O$ (Fig. 4), $H_2O - Me_4NF{\cdot}0.5Pp_4NF{\cdot}15H_2O$ (Fig. 5), and $Pp_4NF{\cdot}11H_2O - Me_4NF{\cdot}0.5Pp_4NF{\cdot}15H_2O$ (Fig. 6) are quasi-binary, have three eutectics, and their melting points are $e_1 = 15.2$°C, $e_2 = -16.0$°C, and $e_3 = -13.6$°C, respectively. In the triangle $Me_4NF - H_2O - Me_4NF{\cdot}0.5Pp_4NF{\cdot}15H_2O$ the melting point of the tertiary eutectic E_1 is -36.9°C,

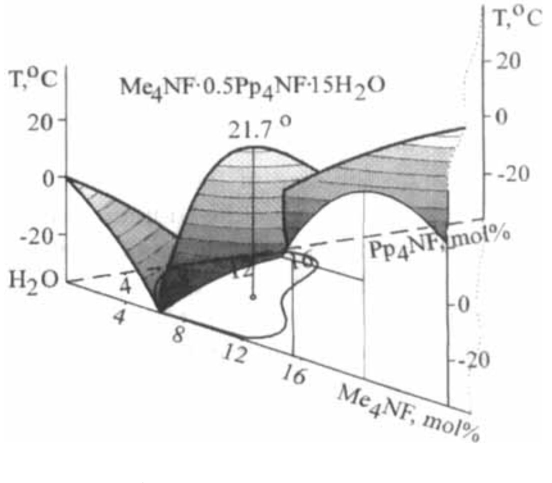

FIGURE 2 A fragment of the spatial phase diagram of the $Me_4NF - Pp_4NF - H_2O$ system.

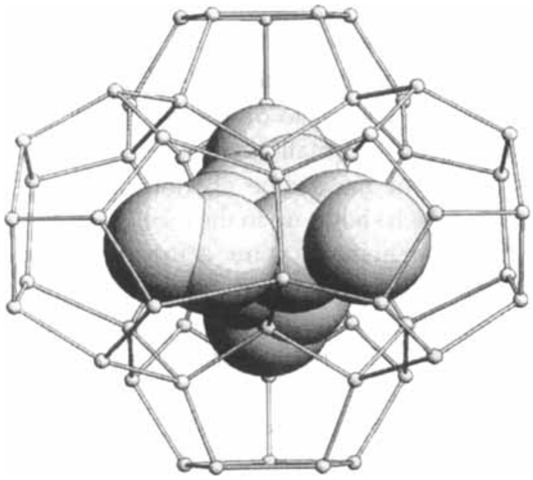

FIGURE 3 Pp_4N^+ cation in 4-section D_4-cavity (hydrogen atoms are omitted), based on molecular modeling.

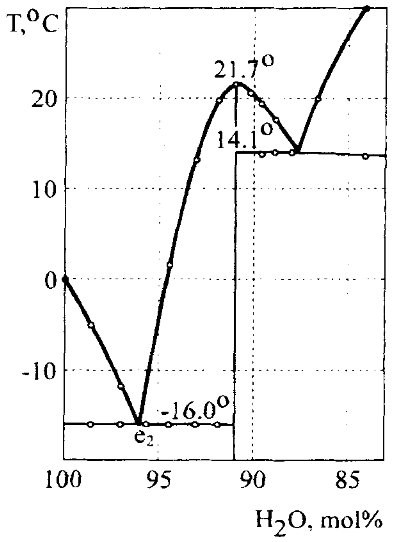

FIGURE 5 Section of the phase diagram of the tertiary system Me_4NF – Pp_4NF – H_2O with the constant molar ratio of the salts Me_4NF:Pp_4NF = 2:1 and variable water content.

which is close to the double eutectic point e_4 at −36.3°C in the diagram Me_4NF – H_2O. In the triangle $Pp_4NF \cdot 15H_2O$ – $Me_4NF \cdot 0.5Pp_4NF \cdot 15H_2O$ – H_2O the tertiary eutectic point E_2 is also located near the eutectic point e_5 in the diagram Pp_4NF – H_2O. The melting points of these two eutectic compositions are −24.2°C for e_5 and −24.4° for E_2.

Using an auxiliary component makes possible formation of solid solutions due to the variable degree of filling of the small cavities. This may either be rather a simple case of solutions with a variable degree of occupation of the small cavities, or quite a complicated case of filling the cavities in blocks with the simultaneous displacing of the framework water molecules by the central cations and anions, as is the case when Pp_4NF is used as an auxiliary component[8]. In

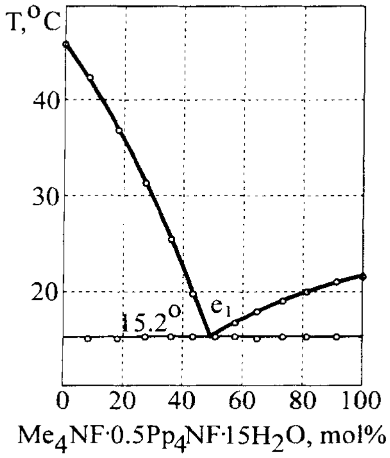

FIGURE 4 Quasi-binary section $Me_4HF \cdot 4H_2O$ – $Me_4NF \cdot 0.5Pp_4NF \cdot 15H_2O$ in the tertiary system Me_4NF – Pp_4NF – H_2O.

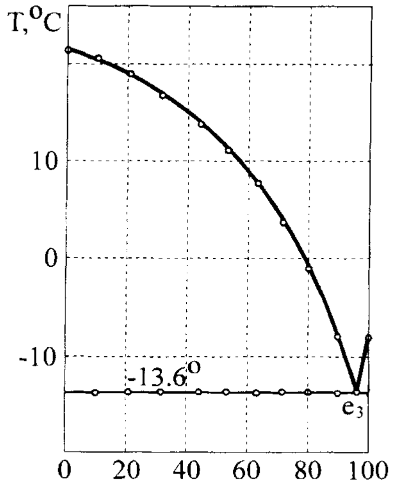

FIGURE 6 Quasi binary section $Me_4NF \cdot 0.5Pp_4NF \cdot 15H_2O$ – $Pp_4NF \cdot 11H_2O$ in the tertiary system Me_4NF – Pp_4NF – H_2O.

contrast to the THF – Pp_4NF – H_2O system, in the Me_4NF – Pp_4NF – H_2O system no formation of solid solutions was observed. This might be due to the fact that there exists no CS-II hydrate $Me_4NF \cdot 16H_2O$ with absolutely empty small cavities. Since the cation Me_4N^+ does not stabilize the large H-cavity, a high degree of filling of the small cavities by the cation Pp_4N^+ is required for the stabilization of CS-II hydrates. Thus, if in the studied range there are solid solutions with a variable degree of occupation of the small cavities, they are located in the narrow range close to 100% filling of the D-cavities.

A study of single crystals by X-ray diffraction shows that this hydrate forms a hexagonal cell with the parameters a = 12.290(5), and c = 59.35(1) Å at −20°C. These parameters point to the hexagonal structure II (HS-II)[1], which was described as an idealized version of the hydrate $(CH_3)_2CHNH_2 \cdot 8H_2O$[10]. CS-II differ from HS-II in the way the layers abcabc in CS-II and the layers abab in HS-II made of dodecahedra alternate. The interrelation between HS-II and CS-II is similar to that between hexagonal and cubic ice. The structure HS-II also has H- and D-cavities, and in this structure, just as in the structure CS-II it is possible to recognize a fragment of tetrahedrally connected 4 D-cavities in which the cation Pp_4N^+ is accommodated. So far no examples of HS-II have been found among hydrates of peralkylammonium salts. Therefore, the hydrate $Me_4NF \cdot 0.5Pp_4NF \cdot 15H_2O$ which we found is the first example of this structure.

The role of entropy and surface energy in choosing the modification for crystals with the dimensions involved is shown[10] by the example of hexagonal and cubic ice and solid noble gases. The case of double CS-II and HS-II clathrate hydrates is undoubtedly more complicated, but the existence of the studied hydrate in the form of CS-II might also be expected. During the X-ray structural analysis we observed a phase transition at −30°C. At temperatures below −30°C the diffraction picture was observed to become more complicated (new reflexions appeared while the peaks characteristic of high temperature modifications were still retained). This process was reversible and temperatures above −30°C caused the additional reflexions to disappear.

Occupation of the small cavities by an additional component makes the clathrate hydrate more stable which shows up in the increase of the double hydrate melting point compared with that of a common hydrate (without an additional component) with the same kind of guest. In the case of the $THF \cdot H_2S \cdot 17H_2O$ hydrate this increase can be as high as 16.4°C, even when the degree of filling of the small cavities is close to 50%. Pp_4NF as an additional component stabilizes the clathrate hydrate to a lesser degree because some energy is spent in the building of the 4-section D_4-cavity[4]. The maximum increase in melting point of the double hydrate (6.6°C) with Pp_4NF used as an auxiliary component is observed for the hydrate $TMO \cdot 0.5Pp_4NF \cdot 16H_2O$ (t_{melt} = −2.6°C) compared to the hydrate $TMO \cdot 17H_2O$ melting point −9.2°C[4]. The melting point of the double hydrate $Me_4NF \cdot 0.5Pp_4NF \cdot 15H_2O$ is 21.7°C and is the highest among the double hydrates studied with Pp_4NF as an auxiliary component. In this case the additional stabilization of the double hydrate relative to the common 1 : 16 hydrate cannot be discussed because in the case of Me_4NF no such hydrate exists. However, mutual stabilization of the main and the additional component in the process of the double clathrate hydrate formation can be assumed. The fact that some clathrate hydrates form only if both the small and large cavities are occupied was found by Ripmeester and Ratcliffe[12]. They found that guests with maximum dimension larger than 7.1 Å require the presence of a help gas to give a stable CS-II hydrate. Molecules whose van der Waals diameter exceeds 7.5 Å (e.g., cyclooctane, adamantane, tetramethylsilane and others) can form only double hydrates provided the small dodecahedral cavities of the hexagonal structure H are occupied (even if they are partially occupied by the additional component molecules. In our case the cation Me_4N^+ is not suitable for the 16-hedral cavity (although its diameter is equal to 6.5 Å) and cannot form the stable HS-II hydrate with vacant dodecahedral cavities.

The density of the double hydrate is 1.091 g·cm^{-3}; and the packing coefficient[12] k = 0.603, determined from the experimental density, is the largest among clathrates with light guests. With the packing coefficient as large as this, an increase in pressure results in the stabilization of the hydrate $Me_4NF \cdot 0.5Pp_4NF \cdot 15H_2O$ (Fig. 7). The hydrate melting point increases from 21.7°C at a pressure of 1 atm. to 59.0°C at 6.75 kbar.

EXPERIMENTAL

Initial aqueous solutions of Pp_4NF and Me_4NF were prepared by an ion exchange reaction of Pp_4NJ and Me_4NI with AgF. Pp_4NF and Me_4NF were recrystallized from aqueous solutions of salts by precipitating the crystals of the hydrates followed by concentration of the product over phosphorous pentoxide in a vacuum-drier. All the solutions used were prepared from the initial solutions and doubly distilled water by weighing. The water content was determined by the Karl Fischer technique with an error 0.6%; Pp_4NF and Me_4NF contents were determined by titration with sodium tetraphenylborate in the presence of a cation selective electrode[12] (error 0.5%). Melting points and solid phase transformations were recorded by the differential thermal analysis method.

Single crystals of the hydrate $Me_4NF \cdot 0.5Pp_4NF \cdot 15H_2O$ were grown from the aqueous solution which contained 6% mol of Me_4NF and 3% mol of Pp_4NF at room temperature. The temperature was regularly made to increase so that it was above the melting point of the crystals for several minutes which resulted in the melting of some crystals. Then temperature was decreased to room temperature. The single crystals obtained in this way had clear-cut faces, were transparent, and octahedral in shape.

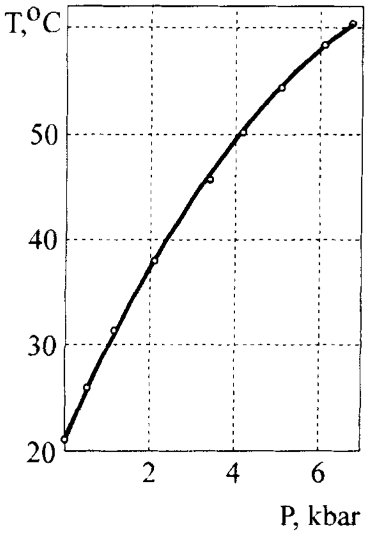

FIGURE 7 Pressure influence on melting point of the double hydrate $Me_4NF \cdot 0.5Pp_4NF \cdot 15H_2O$.

Acknowledgments

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Endnotes

‡ The $4^3 5^6 6^3$ descriptor denotes that the cage is a polyhedron consisting of 3 square, 6 pentagonal and 3 hexagonal faces.