The Formation of Solid Solutions in the Tetrahydrofuran-Tetra(n-propyl)ammonium Fluoride-Water System

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Abstract. The phase diagram of the tetrahydrofuran (THF)-tetra(n-propyl)ammonium fluoride (Prp$_4$ NF)-water system has been studied by differential thermal analysis (DTA). Solid solutions have been detected of the general formula THF $\cdot$ x Prp$_4$NF $\cdot$ $(17-2x)$ H$_2$O, where x changes from 0.06 to 0.5. The formation of solid solutions is due to the variable degree of the filling of the fragment consisting of four D-cavities in CS-II clathrate hydrates by the tetra(n-propyl)ammonium cation. The solid solution obtained is peculiar in that its vacancies are occupied by the blocks of four D-cavities each. Besides, this kind of displacement of two water molecules by an ionic pair Prp$_4$N$^+$+F$^-$, where only the charges of the substituting and substituted groups are equal, takes place here. It appears that this type of solid solution has been discovered for the first time.

Key words: Double clathrate hydrate, solid solutions, tertiary system, tetra(n-propyl)ammonium fluoride.

1. Introduction

As shown in reference [1], tetra(n-propyl)ammonium cation can be introduced hydrophobically into the crystalline frameworks of cubic structure II (CS-II) hydrates, occupying the 4-section cavity D$_4$. Fluoride anion is included in a hydrophilic way, changing the framework from a pure water to a water-anion type. A number of compounds has been obtained [1] with the general formula M $\cdot$ 0.5 Prp$_4$NF $\cdot$ 16 H$_2$O, where M is the molecule of the guest occupying the large cavities. This formula corresponds to the 100% filling of both the small and the large cavities of CS-II hydrates. Prp$_4$NF is here an auxiliary component, which is at present the only known salt which can stabilize the fragment D$_4$ in clathrate hydrates. Marked structural distortions, the change of the 'host' framework caused by Prp$_4$NF, inclusion and its considerable hydration in the solution stabilizing the liquid phase, make Prp$_4$NF less efficient as a stabilizing agent than the 'classical' auxiliary components (H$_2$S, Xe). Thus, the increase of the THF $\cdot$ 0.5 Prp$_4$NF $\cdot$ 16 H$_2$O hydrate melting point relative to that of the THF $\cdot$ 17 H$_2$O hydrate is equal to 3.1°C, while for the THF $\cdot$ H$_2$S $\cdot$ 17 H$_2$O hydrate of the same structure it is 16.4°C

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[2]. (The authors do not present the precise degree of the filling of the small cavities, but judging from the formula given by them it is close to 0.5.) The composition of the double hydrate with tetra(n-propyl)ammonium fluoride in reference [1] does not differ, within the experimental error, from that of the hydrate with 100% filling of the D-cavities. Of all double hydrates of this type, tetrahydrofuran hydrate has been best studied (its melting point is 8.1°C, cubic structure II, $a = 17.67$ Å, density 1.053 g/cm^3 [1]). However, the phase diagram of the tetrahydrofuran-tetra(n-propyl)ammonium fluoride-water system has not been studied at all. The Me$_4$NF-Prp$_4$NF-H$_2$O system has been studied thoroughly [3], and the formation of the double Me$_4$NF $\cdot$ 0.5 Prp$_4$NF $\cdot$ 15 H$_2$O hydrate (a hexagonal structure II, differing from the CS-II structure only by the alteration of the AB and ABC layers, consisting of pentagonal dodecahedra, respectively [4]) has been shown to occur when the filling degree of the D-cavities is equal or very close to 100%. Since the destabilization of tetrahydrofuran hydrate framework by the included fluoride anions is much weaker than that of tetramethylammonium fluoride hydrate, and the guest-guest and guest-host interactions differ from those of tetramethylammonium fluoride hydrate, one can assume that the partial filling of the small cavities is sufficient for the formation of THF $\cdot$ 0.5 Prp$_4$NF $\cdot$ 16 H$_2$O hydrate, i.e. solid solutions can form of the general formula THF $\cdot$ xPrp$_4$NF $\cdot$ (17−2x) H$_2$O, where x changes from the minimum value to 0.5. To study the process of filling the D-cavities in THF $\cdot$ 0.5Prp$_4$NF $\cdot$ 16 H$_2$O hydrate the THF-Prp$_4$NF-H$_2$O system phase diagram has been investigated.

2. Experimental

Tetrahydrofuran was distilled twice and freed from tetrahydrofuran peroxides. The water content was 0.2%, and the index of refraction was 1.4065. Tetra(n-propyl)ammonium fluoride content was determined by the titration of sodium tetraphenylborate with a cation-selective electrode [5]; the experimental error was equal to 0.7%. In the study of the exfoliation isotherm the water content in the samples was determined by the Karl Fischer titration technique; the experimental error was equal to 1%. Solutions of known composition were prepared by weighing; distilled water was used. A hand-made apparatus for differential thermal analysis was used to study the phase diagram. The study at high pressure was carried out on the equipment described in reference [6].

3. Results and Discussion

The phase diagram of the tertiary system in the hydrate formation range was constructed on the basis of 11 polythermal sections studied. The phase diagrams of the THF-H$_2$O and Prp$_4$NF-H$_2$O systems were taken from references [7] and [4]. The scheme does not show the metastable hydrates of the Prp$_4$NF, obtained in reference [4]. A general view of the phase diagram obtained is presented in Figure
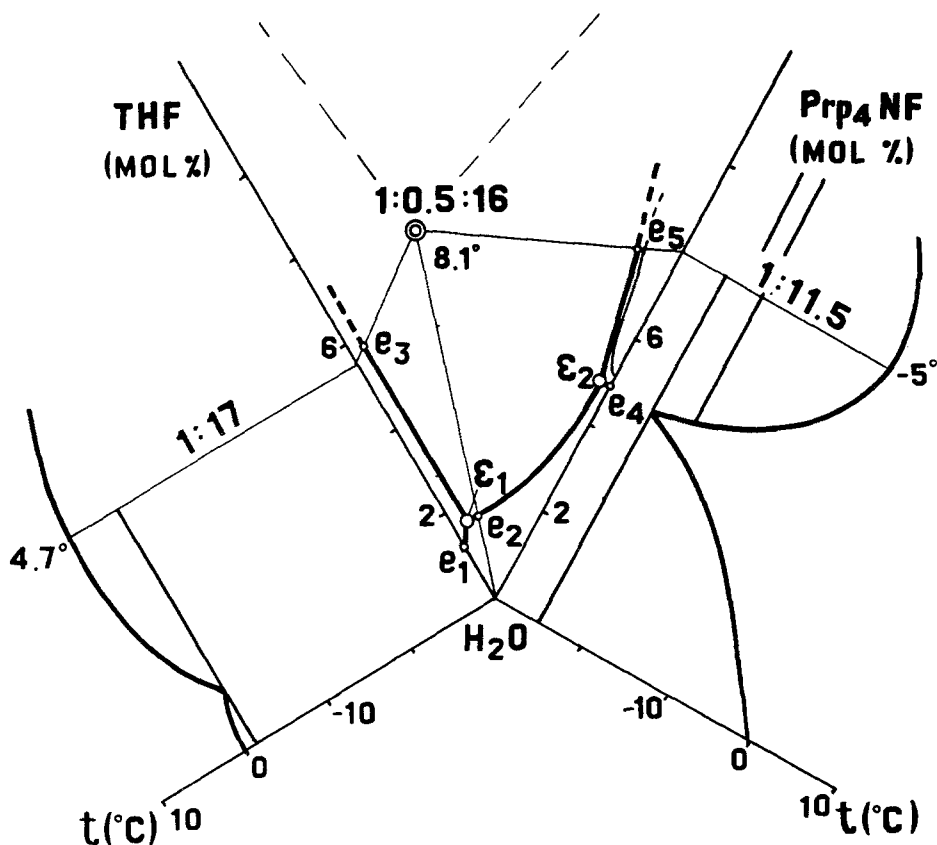
Fig. 1. Phase diagram of the tetrahydrofuran (THF)-tetra(n-propyl)ammonium-water ternary system. Ternary eutectic points are at $-3°C$ (ε_1) and $-27°C$ (ε_2). Eutectics on binary and quasibinary sections: $-1°C$ (e_1), $-3°C$ (e_2), $4.4°C$ (e_3), $-24°C$ (e_4), $-12°C$ (e_5). *Legend*: $1 : 0.5 : 16 = THF \cdot 0.5\ Prp_4NF \cdot 16\ H_2O$; $1 : 17 = THF \cdot 17\ H_2O$; $1 : 11.5 = Prp_4NF \cdot 11.5\ H_2O$.

1. The melting point of the double $THF \cdot 0.5\ Prp_4NF \cdot 16\ H_2O$ hydrate coincides with that obtained in reference [1]. The sections of the $H_2O\text{-}THF \cdot 0.5\ Prp_4NF \cdot 16$ H_2O and $Prp_4NF \cdot 11.5\ H_2O\text{-}THF \cdot 0.5\ Prp_4NF \cdot 16\ H_2O$ systems are quasibinary. The $H_2O\text{-}THF \cdot 0.5\ Prp_4NF \cdot 16\ H_2O\text{-}Prp_4NF \cdot 11.5\ H_2O$ triangle is of the simple eutectic type, with the eutectic (ε_2) melting at $-27°C$. This may be cuased by the presence in the system of a compound which melts incongruently. No specific study of the phenomena has been undertaken. Therefore, the figure illustrates the simplest possible version of the diagram, and the horizontal line is interpreted as a phase transition.

An exfoliation region has been found in the system. Part of it, close to the THF-H₂O edge, has been studied. Figure 2 illustrates two exfoliation isotherms (the isotherm corresponding to 30°C has been constructed on the basis of poly-
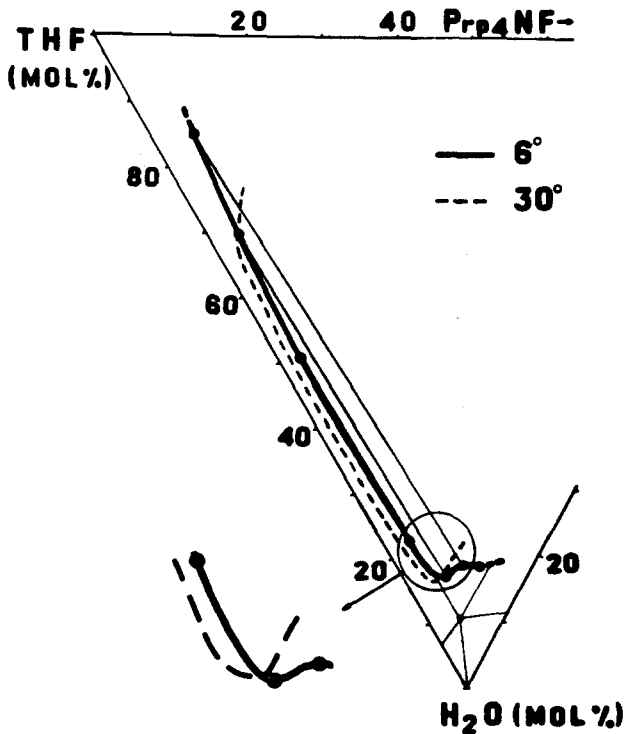
Fig. 2. The part of the exfoliation region studied. The fragment shows the exfoliation isotherm curves, corresponding to the transition from the exfoliation with a reverse solubility course to that with a common solubility course.

thermal sections). The shape of the arc obtained corresponds to the transition from the exfoliation with reverse solubility to that with conventional solubility. This change of the exfoliation type can be explained by the relation between exfoliation and clathrate formation discussed in reference [8]. The THF solution contains the 'debris' of the clathrate hydrate structure, formed by tetrahydrofuran, which stabilizes the solution and is destroyed by heating. As an ionic component is added to and accumulates in the system, these associates decompose due to the attraction of the water molecules to the hydrate shell of the ions. This might be one of the reasons underlying the decrease of the eutectics' melting point at the quasibinary section H_2O-THF $\cdot$ 0.5 $Prp_4NF \cdot$ 16 H_2O relative to the melting point of the water eutectics in the THF-H_2O system.

Two isothermal sections of the diagram in the triangle THF $\cdot$ 17 H_2O-THF $\cdot$ 0.5 $Prp_4NF \cdot$ 16 H_2O-H_2O are shown in Figure 3. The sections were constructed on the basis of the polythermal sections studied; the connodes have been chosen arbitrarily. The faces THF-H_2O and THF $\cdot$ 0.5 $Prp_4NF \cdot$ 16 H_2O-H_2O of this triangle correspond to the eutectic type of diagrams. The section THF $\cdot$ 0.5 $Prp_4NF \cdot$ 16

a) 6°C

THF·17H$_2$O

THF·0.5Prp$_4$NF
;16H$_2$O

H$_2$O   MOL %

b) 4°C

THF·17H$_2$O

H$_2$O   MOL %   THF·0.5Prp$_4$NF
·16H$_2$O
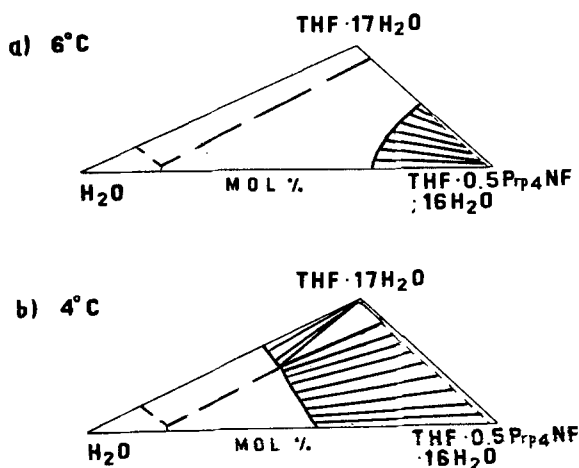
Fig. 3.   Isothermal sections of the diagram of the THF-Prp$_4$NF-H$_2$O system in the triangle
THF · 0.5 Prp$_4$NF · 16 H$_2$O-THF · 17 H$_2$O-H$_2$O. (a) At 6°C; (b) at 4°C.

H$_2$O-THF · 17 H$_2$O is illustrated in Figure 4. According to Roozeboom this corresponds to the type V solid solutions, with a very wide homogeneous region adjacent to the double hydrate. The homogeneous regions of the solid solutions in the triangles THF · 17 H$_2$O-THF · 0.5 Prp$_4$NF · 16 H$_2$O-H$_2$O and THF · 17 H$_2$O-THF · 0.5 Prp$_4$NF · 16 H$_2$O-THF are sketched arbitrarily. According to the diagram these regions appear on the plane of the triangles when the filling degree of the large cavities is less than 100%, which is at variance with the present view [9]. However, there are experimental data on carbon oxide hydrate (cubic structure : I) [10] indicating that when a considerable portion of the small cavities is filled, some of the large ones can remain vacant. The THF-Prp$_4$NF-H$_2$O system might be a convenient model for the study of this problem, using CS-II, because in this structure the small and the large cavities are occupied by different 'guests' and it is experimentally easy to obtain hydrates with high filling degrees of the small cavities.

The slow establishment of the equilibrium resulted in nonequilibrium effects (on the basis of some of these effects and the study of the THF-H$_2$O system one can suggest that the CS-II hydrate exists in the THF-H$_2$O system) hampering the study of the region of solid solution formation. Besides, slight differences in temperatures in this part of the system made it impossible to confirm our assumption on the type of the diagram. To refine the type of the diagram in the region where we assume that solid solutions form, we studied the dependence of dT/dP vs. composition (dT/dP-dT/dP value for melting curve of the sample at 1 atm) for samples located on the section THF · 17 H$_2$O-THF · 0.5 Prp$_4$NF · 16 H$_2$O (the value of dT/dP on this section changes from -2.7 K/kbar for THF · 17 H$_2$O to 10 K/kbar for THF · 0.5 Prp$_4$NF · 16 H$_2$O).
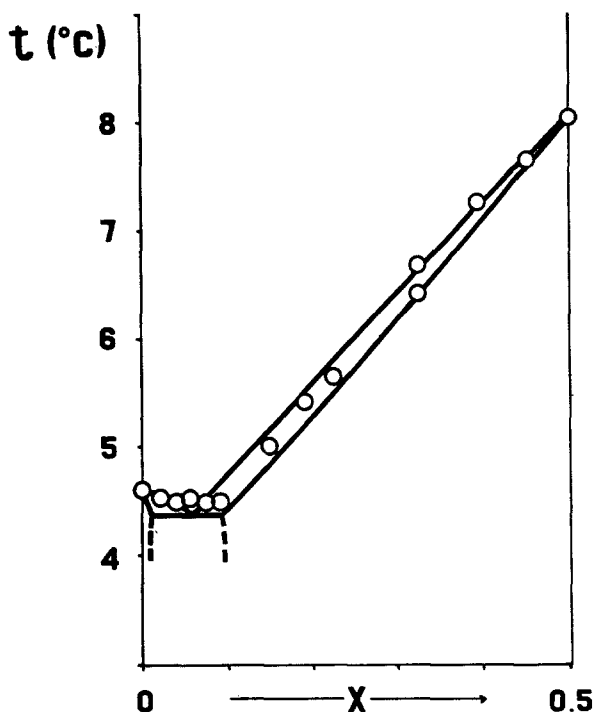
Fig. 4.   Polythermal section of the THF · 0.5 Prp₄NF · 16 H₂O-THF · 17 H₂O phase diagram of the THF-Prp₄NF-H₂O system. The composition of this section corresponds to the general formula THF · xPrp₄NF · (17−2x) H₂O. The value of x is plotted on the X axis.

The preliminary analysis of the curves of dT/dP vs. composition showed that in the case of the eutectic type of diagrams (with or without solid solutions) in the eutectic point one can usually observe a disruption, or, occasionally, as a special case, a fracture. This relationship is illustrated in Figure 4. Insufficient experimental accuracy does not allow us to accurately determine the shape of the curve, but the diagram with the disruption at the composition point THF · 0.06 Prp₄NF · 16.88 H₂O seems to be the most likely. Thus, on the basis of the differential thermal analysis data and the study of the behaviour of the compositions under pressure one can conclude that the type of diagram which we have assumed is the most probable one.

The solid solutions obtained are peculiar in that they can be rightly considered to belong to both inclusion solid solutions and displacement solid solutions. Cases of displacement of this kind, where the charges of the displacing and the displaced particles do not equal each other, are well known (only total charges of the displacing and the displaced ionic pairs are the same here). In this case the place of two uncharged water molecules is occupied by the ionic pair Prp₄N⁺+F⁻. Cases where the molecule which is included occupies a block of several vacant cavities

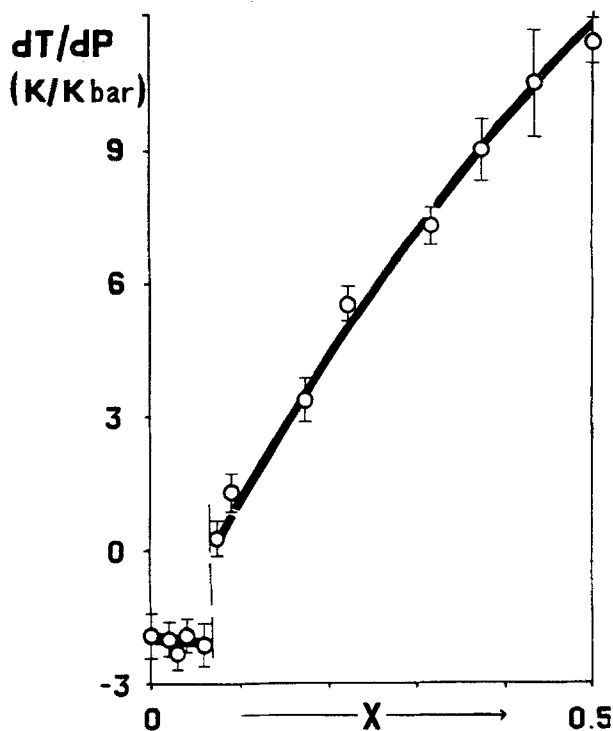Fig. 5. The dependence of the value of dT/dP of the compositions of the general formula THF $\cdot$ xPrp₄NF $\cdot$ $(17-2x)$ H₂O upon the value of x. One can see that the point of the curve's disruption corresponds to the point of the eutectics on the polythermal section assumed.

in a stable structure are much less frequent. Ionic solid solutions of this kind are well known. Thus, in the NH₄Cl-MnCl₂-H₂O system the (MnCl₄ $\cdot$ 2 H₂O)²⁻ block displaces the (2NH₄Cl+2Cl⁻) group [11], and a number of similar systems is described in reference [12]. However, in clathrate chemistry this seems to be the first case of this type of solid solutions known, because Prp₄NF is now the only example of a tetraalkylammonium cation being introduced into the stable clathrate hydrate framework in which the large cavities are occupied (though similar solid solutions formed by the molecules occupying 1 D-cavities occur frequently). Clathrate hydrates of tetraalkylammonium salts with cations occupying the large cavities have been studied thoroughly and are considered to be stoichiometric compounds [9].

The conditions under which solid solutions similar to those discussed above can be obtained and might be met by the combination of the conditions necessary for obtaining displacement and inclusion solid solutions. The most important conditions are the similarity of the volumes of the anion and water molecule and of the bonds formed between them, and the resemblance of the geometry of the cation to that of the vacant cavities. The stability of the initial hydrate is also very important.

Acknowledgements

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