[September, 1980] © 1980 The Chemical Society of Japan *Bull. Chem. Soc. Jpn.*, **53**, 2427—2433 (1980) 2427

Hydrates of Organic Compounds. V. The Clathrate Hydration of Alcohols

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(Received November 27, 1979)

A new method for examining the ability of a given substance to form a hydrate with the same structure as that of a reference substance has been established. By using this method, for a series of alcohols ranging from methyl alcohol to pentyl alcohol, including their isomers, the ability to form a clathrate hydrate of either Structure I or Structure II has been investigated. It has been found that: (1) methyl alcohol has the ability to form both Structure I and II hydrates; (2) ethyl alcohol has the ability to form a Structure II hydrate; (3) all C_3-alcohols (propyl, isopropyl, allyl, and propargyl alcohol) can actually form Structure II hydrates with relatively high (around -10 °C) incongruent melting points, and (4) among the C_4- and C_5-alcohols, only *t*-butyl alcohol has the ability to form a Structure II hydrate. However, it is uncertain for methyl and ethyl alcohols whether they actually can form such hydrates even in the absence of a reference substance. These results strongly suggest that the size and/or shape limitation plays an important role in the formation of alcohol hydrates with a gas-hydrate structure, just as has been found for the formation of ether and ketone hydrates.

A group of polar substances, such as ethers (dimethyl ether,[1–3] tetrahydrofuran,[1,4–9] ethylene oxide,[1,8,9] 2,5-dihydrofuran,[4–6,9] propylene oxide,[4–6,9] trimethylene oxide,[4–6,9] and 1,3-dioxolane[5,6,9,10]) or ketones (cyclobutanone[5,6,11] and acetone[12–14]), are new known to form so-called "gas hydrates" with von Stackelberg's Structures I and II,[15] in which hydrogen-bonded water molecules form host lattices with specific polyhedral voids, such as tetrakaidecahedron and hexakaidecahedron.

Among a group of polar substances whose clathrate hydration has not been extensively studied is a series of alcohols. The formation of a solid different from ordinary ice in concentrated aqueous solutions of alcohols (such as ethyl alcohol, propyl alcohol, isopropyl alcohol, and allyl alcohol) was reported as early as 1896,[16] and later works have also suggested the existence of ethyl alcohol hydrate.[17] An extensive study by Potts *et al.*[18] in 1965 showed the existence of an ethyl alcohol hydrate below -73.5 °C. Its composition was near $C_2H_5OH \cdot 17H_2O$, similar to the Structure-II gas hydrates. On the other hand, from crystallographic studies Sargent *et al.*[5] concluded that the hydrate formed in the $C_2H_5OH+H_2O$ system was not Type II, and Calvert *et al.*[19] showed that there were more than one hydrate: Type I, with a structural disorder similar to that of ethylene oxide hydrate, and a modified Type II hydrate. Thus, even now there is some uncertainty concerning the structure and properties of ethyl alcohol hydrate. Of the other alcohols, though some irregular behavior has been found in the phase diagrams of alcohol+water binary systems,[20,21] no clathrate hydration has so far been reported.

In this investigation, in order to identify the clathrate hydration of alcohols phase-diagrammatically, we made use of the phenomenon of the "mixed hydrate" formation of alcohols with a reference substance like tetrahydrofuran. Since Structure II hydrates are exclusively formed by molecules with diameters in the range of 5.6—6.6 Å,[22] and since the molecular diameters of the alcohols examined in this study, except for methyl alcohol, are greater than 6 Å, we will primarily discuss the formation of a hydrate of Structure II except for the case of the clathration of methyl alcohol. In Structure II hydrates, as is also true in Structure I hydrates, the structures of the hydrogen-bonded water frameworks are all essentially the same, apart from a slight distortion caused by the nature of the individual guest molecule; they comprize an iso-structural series with similar unit-cell dimensions[5] and crystal symmetry. Thus, it can be anticipated that, when two components have molecules of a size that form Structure II hydrates, a solid solution which has an intermediate decomposition temperature will be formed by mixing them. In reality, the formation of a solid solution of this kind has already been confirmed in several systems.[23–25]

Another striking feature possessed by these hydrates is that the guest molecules nearly fully occupy large voids (16-hedra in Structure II hydrate). This means that most of these hydrates are stoichiometric[22] and that, therefore, the composition of Structure II hydrate is close to $M \cdot 17H_2O$, in which M stands for the guest molecule. From these considerations, it can reasonably be anticipated that the mixed hydrate formed from a binary-liquid mixture of $M+M'$, each component of which can form, for example, a Structure II hydrate ($M \cdot 17H_2O$ and $M' \cdot 17H_2O$), will have properties characteristic of a solid solution with complete miscibility and will be expressed by the $(M)_\alpha(M')_{1-\alpha} \cdot 17H_2O$ formula. Each 16-hedron will be occupied by either M or M′, and the relative content of the two will be varied continuously with the change in the conditions, such as the temperature and the composition of the mixture from which the solid solution is formed.

We have developed a new method which enables us to conclude whether one substance M′ can form a hydrate with the same structure as that of M by examining a solid-liquid-phase diagram of a ternary mixture of $M+M'+$water prepared under specific conditions. Palmer *et al.*[23] also selected, as a criterion for hydrocarbon-type hydrates, the condition that hydrates of mixtures exhibit behavior typical of soild solutions. However, their conclusions, derived from thermal analyses, are not in agreement with the facts found in subsequent experiments; their method, for example, cannot lead to the fact that acetone forms a Structure II hydrate.

Experimental

Procedure. The procedure is summarized as follows: (1) A substance which has been known to form a congruently melting hydrate of a known structure is chosen as the reference component, M. It is preferable that its congruent melting point be as high as possible. (2) A solid is formed from a series of mixtures of various compositions X $(=X_{\mathrm{M}}+X_{\mathrm{M}'})$, with the restriction that the $X_{\mathrm{M}}:X_{\mathrm{M}'}$ ratio is kept constant, where X_{M} and $X_{\mathrm{M}'}$, are the mole fractions of M and M′ respectively. (3) For a series of the solids, the temperature (T) at which the solid phase completely disappears is observed and is plotted against X. (4) If the value of X which gives a maximum temperature in the T-X plot for a series of mixtures is independent of the molar ratio, $X_{\mathrm{M}}:X_{\mathrm{M}'}$, and is the same as that found for the binary mixture, M+water, we may conclude that the M′ component has at least the ability to form a hydrate of the same structure as that of M, since such behavior should be observed only when a solid solution is formed between M-hydrate and M′-hydrate. In this investigation, as a reference substance (M) we chose tetrahydrofuran (which is abbreviated by THF hereafter) for a Structure II hydrate and ethylene oxide (EO) for a Structure I hydrate.

Materials and Measurements. All the organic reagents used in this report, except for ethylene oxide, were extra-pure reagent-grade and were purified by conventional methods. The ethylene oxide was kindly supplied by the Nihon Shokubai Co., Ltd., and was used without further purification. The water was doubly distilled in an all-Pyrex still. Ternary mixtures of an alcohol, either tetrahydrofuran or ethylene oxide, and water were made up by weight. No attempt was made to remove the air dissolved in the solution. Each solution (about 1—2 cm^3) was sealed in a small glass ampoule and was cooled until the solid phase appeared. Then the ampoule was gradually warmed and was kept standing for more than 10 h at a temperature several degrees lower than its approximate dissolving temperature (which had been determined by a preliminary survey) in order to obtain a well-grown solid phase in equilibrium with its solution phase. Then the ampoule was slowly warmed again (at the rate of 0.2—0.3 °C/h), with frequent shaking in a constant-temperature bath. The solid-liquid-phase diagrams were determined by measuring the temperature at which the solid phase completely disappeared. Such methods as cooling-curve measurements and temperature and calorimetric measurements by the use of a differential scanning calorimeter (Shimadzu Seisakusho, SC-20) were also employed when necessary. In order to confirm the conclusion obtained from the phase-diagrammatic behavior, the approximate content of the alcohol existing in a solid phase, as well as those of tetrahydrofuran and water, was determined by means of gas chromatography (Shimadzu Seisakusho, GC-4APT), using either a 1-m polyethylene glycol column at 60 °C or a 3-m diglycerol column at 100 °C, with a flow rate of the carrier gas (He) of 40 cm^3/min.

Results and Discussion

Confirmation of Validity of the Method. First, in order to test the validity of our method, we obtained the T-X plots for systems containing M′, which had previously been established to form a Structure II hydrate. In Fig. 1 the T-X plots are shown for the THF+1,3-dioxolane system. The 1,3-dioxolane molecule is another example whose hydrate is Structure II and which has a congruent melting point.[5,6,9,10] The top curve (marked with 1:0) and the bottom curve (marked with 0:1) indicate the solid-liquid-phase diagrams of binary mixtures of THF+water and 1,3-dioxolane+water respectively. These two curves clearly show the formation of the THF hydrate and the 1,3-dioxolane hydrate, both of which have a hydration number of 17 (X=1/18=0.056), characteristic of a Structure II hydrate. The observed congruent melting points of these hydrates (5.1 °C for the THF hydrate and −1.5 °C for the 1,3-dioxolane hydrate) are somewhat different from the reported values (4.38 °C[26] and 5.1 °C[4] for the THF hydrate; −5 °C[5] and −3 °C[10] for the 1,3-dioxolane hydrate). This discrepancy may be due to the presence of air in the hydrate, as has often been pointed out.[7] The absolute value of the melting point, however, does not have any influence on the analyses below. The other three curves in Fig. 1 are T-X plots for systems in which the molar ratios of THF:1,3-dioxolane are 1:1, 1:3, and 1:9. It is noteworthy that the dotted line which connects the points of the highest temperature in each curve is vertical around X=0.056, which corresponds to a hydration number of 17. This behavior is exactly the same as was anticipated in the above discussion.

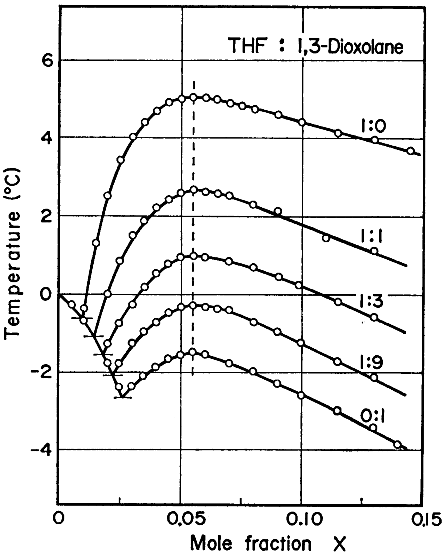

Fig. 1. The solid-liquid-phase diagrams for the THF +1,3-dioxolane+water systems.
The temperatures at which solid phase completely disappears are plotted against total mole fraction (X) of THF and of 1,3-dioxolane. The ratio attached to each curve indicates the molar ratio of THF:1,3-dioxolane in the original solution. Thus the curve marked with 1:0 is a solid-liquid equilibrium curve for THF+water binary system and one with 0:1 is that for 1,3-dioxolane+water binary system. All the following figures are made in a similar manner.

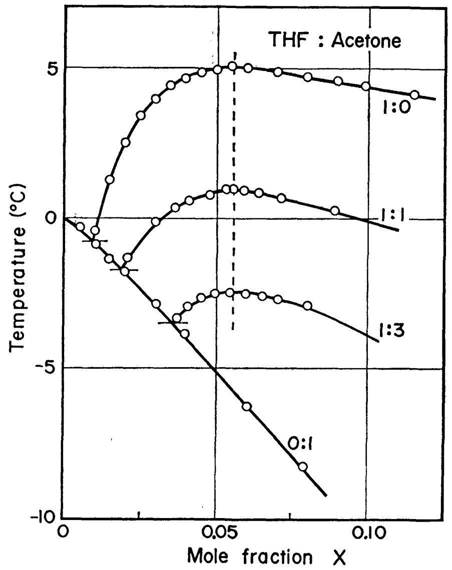

Fig. 2. The solid-liquid-phase diagrams for THF+acetone+water systems.
Explanations are given in Fig. 1.

Analogous plots for the THF+acetone system are shown in Fig. 2. Since acetone forms a Structure II hydrate with an incongruent melting point (−19.8 °C[11]), we cannot, of course, observe a peak at X=0.056 in the T-X plots for the acetone+water binary system. Only an ice-solution equilibrium curve can be obtained at a temperature higher than its incongruent melting point. However, Fig. 2 clearly shows that the T-X plots for mixtures of acetone with THF behave in the same manner as in the case shown in Fig. 1. The X which corresponds to a maximum temperature in each curve is independent of the molar ratio of THF: acetone and is around 0.056, as expected. This indicates that our principle can also be applied to a component which forms an incongruently melting hydrate. As can obviously be seen from Figs. 1 and 2, the maximum temperature in each mixture is quite high as compared with the one calculated from the proportional distribution of the melting points of both hydrates on the molar-ratio basis. This is presumably due to an enrichment of one component with a high melting point in the solid phase, as is often observed in completely miscible solid–solution systems. This effect provides a suitable condition for a temperature peak to appear beyond an ice-solution equilibrium curve, as is exemplified in Fig. 2 and in many other systems to be discussed later.

Figure 3 shows similar T-X plots for the system of THF+diethylene glycol dimethyl ether (DGDME). The latter component, which is too large to form a Structure II hydrate, was deliberately chosen in order to see the phase-diagrammatic behavior of a mixture of a hydrate former+a hydrate non-former. Figure 3 clearly shows different behavior from that found in hydrate former+hydrate former mixtures, as shown in Figs. 1 and 2; the X's which give the maximum temperatures (connected with a dotted line) depend on the THF:DGDME ratio and decrease with an increase in the DGDME content. This may be interpreted as a result of the much-depressed activities of the water molecule due to a strong interaction between water and DGDME, which is partly exemplified by the ice-solution equilibrium curve of the binary DGDME+water system. The decrease in the maximum temperature with the increase in the DGDME content may be simply interpreted as a melting-point depression of the THF hydrate upon the addition of DGDME.

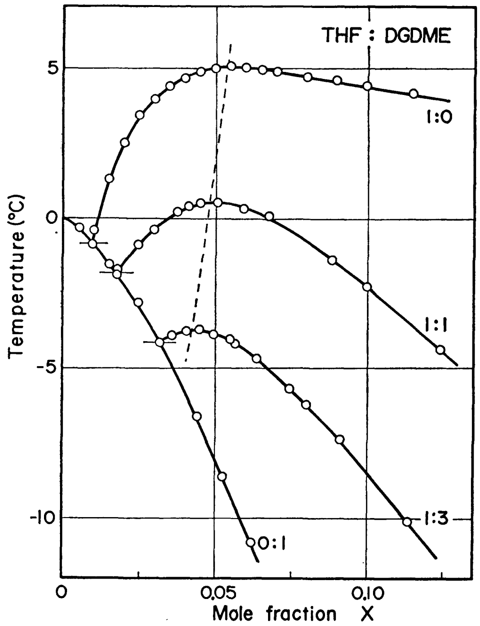

Fig. 3. The solid-liquid-phase diagrams for THF+diethylene glycol dimethyl ether+water systems.
Explanations are given in Fig. 1.

From these confirmations, we may certainly conclude that the procedure employed in this report can provide information about whether or not a given substance has the ability to form a hydrate with the same structure as that of a reference substance.

Ethyl and C_3-Alcohol Hydrates. In view of the fact that the size and/or the shape of the guest species are/is the most important factor for the formation of the hydrate with a gas-hydrate structure, ethyl alcohol and a variety of C_3-alcohols are compounds which can be expected to very likely form a Structure II hydrate. The T-X plots for the systems of THF+ethyl alcohol, THF+propyl alcohol, THF+isopropyl alcohol, THF+allyl alcohol, and THF+propargyl alcohol are shown in Figs. 4—6. Despite the rather intricate discussion of the formation of ethyl alcohol hydrate with Structure II presented in an earlier section, the results shown in Fig. 4 clearly indicate that ethyl alcohol has the ability to form a Structure II hydrate with an incongruent melting point. Although it is impossible to estimate the exact value of the incongruent melting point, it is certain, by a comparison of Fig. 4 with Fig. 2, that it is considerably lower than that of acetone hydrate (−19.8 °C[11]).

As may be seen from Figs. 4—6, all the C_3-alcohols behave in a similar manner: (1) in each mixture

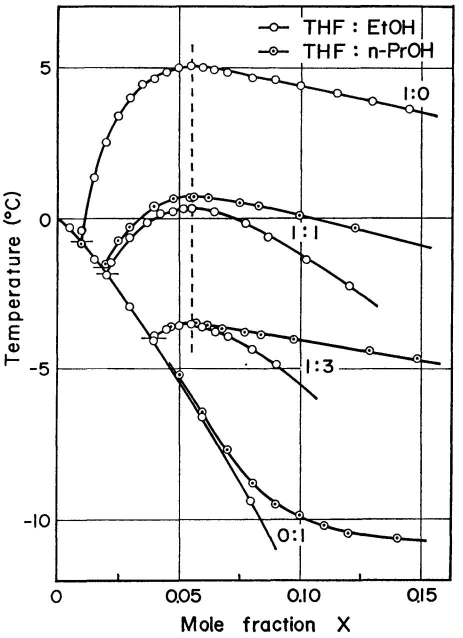

Fig. 4. The solid-liquid-phase diagrams for THF+ethyl alcohol+water systems (—○—) and THF+propyl alcohol+water systems (—⊙—). Explanations are given in Fig. 1.

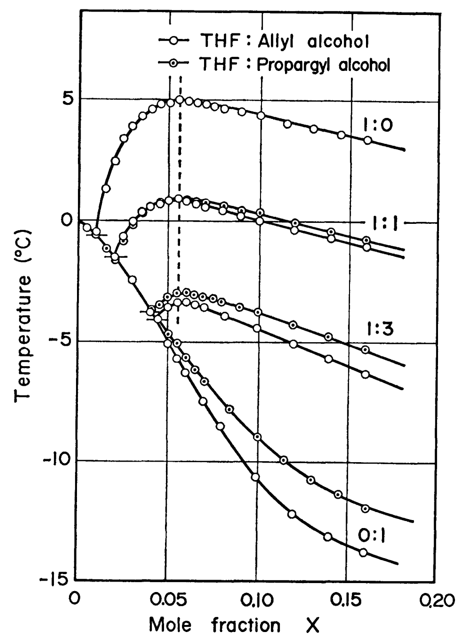

Fig. 6. The solid-liquid-phase diagrams for THF+allyl alcohol+water systems (—○—) and THF+propargyl alcohol+water systems (—⊙—). Explanations are given in Fig. 1.

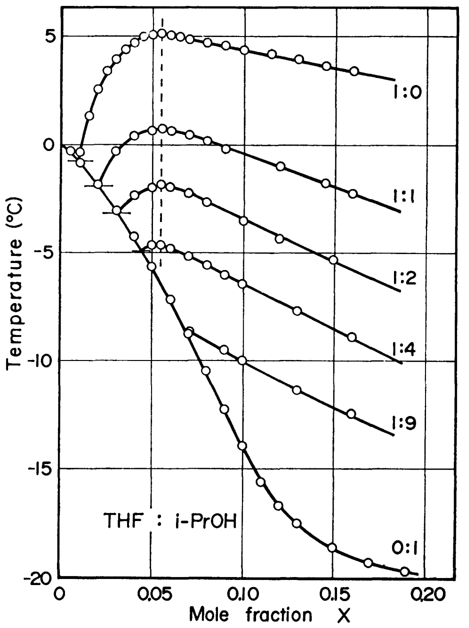

Fig. 5. The solid-liquid-phase diagrams for THF+isopropyl alcohol+water systems. Explanations are given in Fig. 1.

with THF, the X's corresponding to the maximum temperature have the same value, around 0.056, within the limits of experimental error; (2) in each binary mixture of the alcohol+water, the equilibrium curve (marked with 0:1) bends at around −10 °C for propyl, allyl, and propargyl alcohols and at about −18 °C for isopropyl alcohol. Both of these phenomena suggest that all the C_3-alcohols can form hydrates of the Structure II type. In fact, thermal analysis by means of a differential scanning calorimeter also revealed that the solid made by cooling the alcohol+water binary mixture showed a marked absorption of heat at about −11 °C for propyl alcohol, −16 °C for isopropyl alcohol, −12 °C for allyl alcohol, and −10 °C for propargyl alcohol when each solid was gradually heated. These temperatures seem to correspond to the incongruent melting point of each alcohol hydrate. In addition, more elaborate thermal analyses[30] for the propyl alcohol+water system strongly indicated that the hydration number of the propyl alcohol hydrate was 17 (Structure II). As far as we know, no formation of a C_3-alcohol hydrate with a Structure II has been reported explicitly. It is noteworthy that the incongruent melting points of these C_3-alcohol hydrates are surprisingly high as compared with that of the ethyl alcohol hydrate reported by Potts *et al.* (−73.5 °C[18]).

C_4- and C_5-Alcohols. From the standpoint of size and/or shape limitations of a guest molecule on the formation of a Structure II hydrate, it seems to be difficult for C_4-alcohols to form such hydrates. In fact, there exists no proof for its formation. The T-X plots for the THF+*t*-butyl alcohol (TBA)+water mixtures are shown in Fig. 7. The solid-liquid equilibrium curve (marked with 0:1) for the TBA+water binary system clearly shows no formation of a hydrate of Type II. The solid phase formed at high concentrations (above X=0.064) seems to be $TBA\cdot 2H_2O$, as was pointed out by Ross.[20] The T-X plots for ternary mixture of THF+TBA+water, however, behave in a manner similar to that in the systems containing ethyl alcohol and C_3-alcohols (Figs. 4—6); each T-X curve for these systems has a maximum temperature at X=0.056. Thus, from our criterion, it may be concluded that the TBA molecule has the

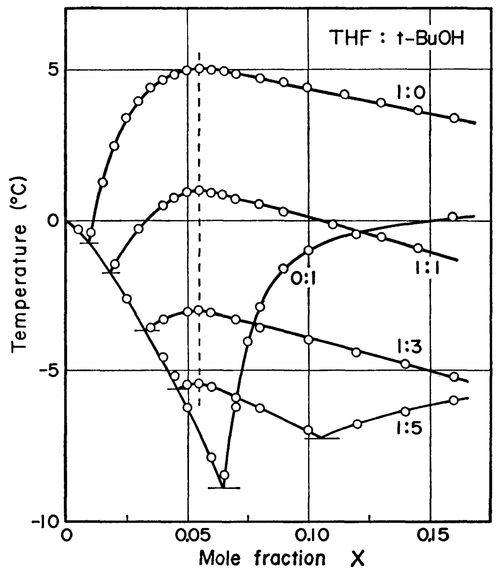

Fig. 7. The solid-liquid-phase diagrams for THF+*t*-butyl alcohol+water systems.
Explanations are given in Fig. 1.

ability to form a Structure II hydrate. Chemical analysis by means of gas chromatography also shows that the TBA molecule exists in the solid phase formed from such a ternary mixture. This can be interpreted by the following considerations. Although the TBA molecule cannot form a stable Structure II hydrate by itself because of its molecular diameter is a little larger than the limiting value of 6.6 Å, the lattice distortion caused by the TBA molecule is not so severe that the formation of a solid solution of a Structure II hydrate containing TBA is possible by incorporating the THF molecule as much as possible. The fact that TBA can form a double hydrate (Structure II) with H_2S,[31] $TBA \cdot 2H_2S \cdot 17H_2O$, gives other evidence in support of the slight distortion effect of the TBA molecule on the water structure: in this hydrate the stabilization due to the occupation of the H_2S molecule in vacant 12-hedra seems to overcome the unfavorable distortion effect of the TBA molecule.

The behavior of the *T*-*X* plots for the other three C_4-alcohols (butyl, isobutyl, and *s*-butyl alcohols) is quite different from that shown in Figs. 4—7. As an example, the *T*-*X* plots for the THF+butyl alcohol+water system are illustrated in Fig. 8. Because of the low solubility of butyl alcohol in water, the equilibrium curve (marked with 0:1) for the binary mixture with water shows the existence of a two-liquid-phase region and shows no indication of the formation of a Structure II hydrate. In Fig. 8, only the *T*-*X* plot for an equimolar mixture of THF+butyl alcohol is shown. Two liquid phases also exist in the region between two dotted lines. It is noteworthy that the 1:1 curve has quite a broad peak around *X*=0.25: this is quite different from the value corresponding to the THF+water system (0.056), indicating that the butyl alcohol does not have the ability to form a Structure II hydrate at all. The behavior of this 1:1 curve can be interpreted as follows: the solid phase formed is a simple THF hydrate (its melting point is depressed by the existence of butyl alcohol), and a high THF concentration is needed to maintain the THF hydrate in the solution since a considerable amount of THF is either distributed between the two liquid phases or extracted by liquid phase containing a large amount of butyl alcohol. The analysis by means of gas chromatography indicates, for example, for the system of *X*=0.14 (two liquid region) which is kept at 1.1 °C, that the molar ratio of THF:butyl alcohol:water is 1:0.04:18 for a solid sample separated from the liquid phase (the small amount of butyl alcohol may be ascribed to the incorporation of the mother liquid), 1:2.0:7.0 for an upper-liquid phase, and 1:0.75:2.2 for a lower-liquid phase (the volumes of the two phases are almost the same, and a small amount of the solid phase wafts in the upper portion of the lower-liquid phase). These results strongly support the above anticipation.

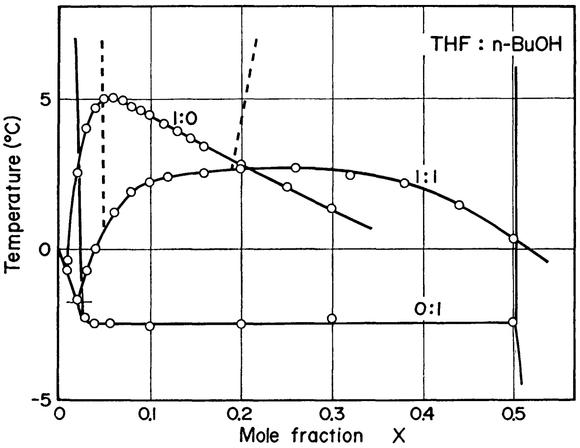

Fig. 8. The solid-liquid-phase diagrams for THF+butyl alcohol+water systems.
Explanations are given in Fig. 1.

All the *T*-*X* plots for ternary mixtures of THF+C_5-alcohol+water also showed the same behavior, as is shown in Fig. 8.

Methyl Alcohol Hydrates. Since the molecular diameter of methyl alcohol is around 5.2—5.3 Å,[22] we first examined the possibility of the formation of a methyl alcohol hydrate of Structure I by using ethylene oxide (EO) as the reference substance. It has been known that ethylene oxide hydrate[27—29] is a Structure I with a congruent melting point of 11.1 °C.[27] The *T*-*X* plots for the EO+methyl alcohol+water system are shown in Fig. 9. The solid-liquid equilibrium curve (marked with 1:0) for the EO+water binary system was taken from the literature.[27] Three *T*-*X* curves (marked with 1:1, 1:3, and 1:5) for the ternary mixtures show the same behavior as in Figs. 4—7, indicating that methyl alcohol has the ability to form a Structure I hydrate. It is uncertain, however, whether methyl alcohol can actually form a Structure I hydrate without the assistance of EO.

On the other hand, the *T*-*X* plots for the ternary mixture of THF+methyl alcohol+water, shown in Fig. 10, also show that the methyl alcohol hydrate can form a solid solution with a THF hydrate of Struc-

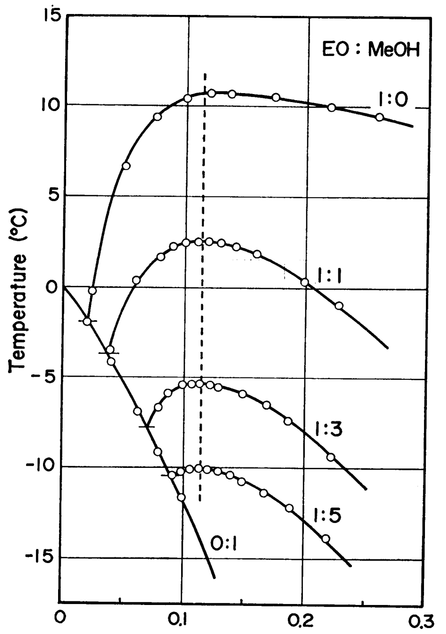

Fig. 9. The solid-liquid-phase diagrams for ethylene oxide+methyl alcohol+water systems. Explanations are given in Fig. 1.

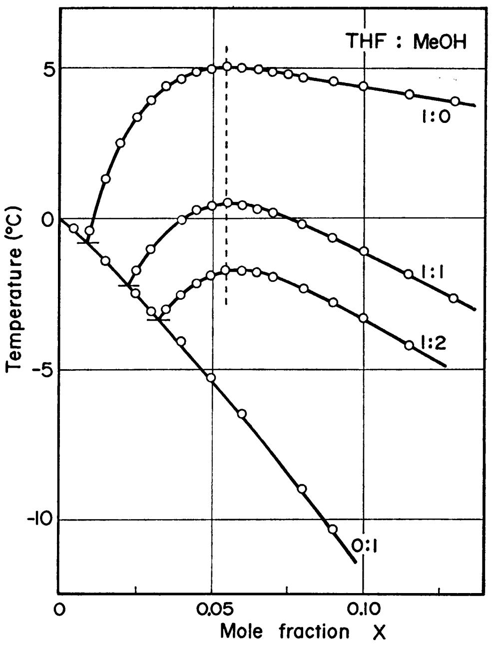

Fig. 10. The solid-liquid-phase diagrams for THF+methyl alcohol+water systems. Explanations are given in Fig. 1.

ture II. Gas chromatographic analysis also supports this conclusion. For example, the molar ratio of THF:methyl alcohol:water is 1.0:0.85:31.0 for the solid phase formed from a solution containing X=0.07 (the molar ratio of THF:methyl alcohol is 1:3) and kept at −10.3 °C. This composition can reasonably be explained by looking upon the solid phase as a mixture of 1 mol of the THF·17H_2O hydrate and 0.85 mol of the MeOH·17H_2O, hydrate. However, this Structure II hydrate, MeOH·17H_2O, seems to be found only when a suitable other molecule such as THF coexists with methyl alcohol, since the methyl alcohol is not large enough to stabilize a Structure II hydrate by itself: stable Structure II hydrates are formed for guest molecules of 5.6—6.6 Å, as has been mentioned earlier.[22)]

Summary. From these results we may classify the series of alcohols into the following four groups: (1) methyl and ethyl alcohol—these alcohols have at least the potential ability to form clathrate hydrates of either Structure I (for methyl alcohol) or Structure II (for both alcohols). It is uncertain, however, whether they can actually form such hydrates from the alcohol+water binary mixtures alone; (2) propyl, isopropyl, allyl, and propargyl alcohol—all these C_3-alcohols can form a Structure II hydrate with relatively high incongruent melting points around −10 °C; (3) *t*-butyl alcohol—though this alcohol has the potential ability to form a Structure II hydrate, it cannot form such a hydrate from the *t*-butyl alcohol+water mixture alone; and (4) other C_4- and C_5-alcohols—these alcohols do not have any potential possibilities to form the hydrates of the gas-hydrate type. These results strongly support the idea that the size and/or shape of a guest molecule also plays an important role in the formation of alcohol hydrates of Structure I and II, just as in the case of ether and ketone hydrates, and further, that the existence of a polar OH group has little influence on their formation. It is noteworthy that the experimental method employed in this study can also be applied to any other types of clathrate hydrates.

The authors wish to express their thanks to Mr. Manabu Sakai and Mr. Akira Kaneko for their preliminary experiments.

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