Hydrates of Organic Compound IX. Enclathration of Methyl and Ethyl Alcohols within the Water Lattice of Tetrahydrofuran Clathrate Hydrate

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Synopsis. The amount of methyl or ethyl alcohol existing in a hydrate solid deposited from ternary mixtures of methyl (or ethyl) alcohol-tetrahydrofuran-water has been determined using ^{14}C-labeled alcohols. It was found that these alcohols could be enclathrated within the water lattice of tetrahydrofuran clathrate hydrate.

In a previous paper[1] a phase-diagrammatic method for examining the ability of an alcohol to form a clathrate-like hydrate in the presence of a reference substance, ethylene oxide or tetrahydrofuran, has been proposed and it has been concluded that both methyl and ethyl alcohols can be enclathrated within the water lattice of tetrahydrofuran(THF) hydrate (Type II). However, this method may lead to a wrong conclusion in some cases, especially when (1) a peak position in a phase diagram is obscured because of the flatness of the peak and (2) the peak position does not apparently shift owing to a complicated change of activity coefficients of the components concerned with their concentrations.[2] In fact, some other measurements have concluded that methyl alcohol cannot be enclathrated within the water lattice of such hydrates as ethylene oxide and THF.[2]

The purpose of this paper is, therefore, to carry out a direct measurement of the amount of either methyl or ethyl alcohol present in the solid carefully formed from a ternary mixture of the alcohol-THF-water by using radioactive alcohols.

Experimental

Procedure and Measurements. A mixture (about 10 g) containing given amount of either methyl or ethyl alcohol (^{14}C-labeled, 0.1—0.3 μCi), tetrahydrofuran(THF), and water was prepared. The mixture was inserted into one portion of a forked glass vessel, and cooled until the solid phase appeared. It was then gradually warmed until only a small amount of the solid remained undissolved. Then the mixture was kept standing for more than 12 h at an appropriate temperature mentioned below in order to grow the solid as slowly as possible.

A known amount (0.5—3 g) of the solid sample, which was separated from its supernatant solution by filtration, was dissolved in a given amount of scintillator, Insta-gel (Packard Instrument Co., Inc.). The radio activity of the sample was measured using the TRI-CARB 460C Automatic Liquid Scintillation System (Packard Instrument Co., Inc.).

Determination of the Experimental Conditions. In Fig. 1, the solid-liquid phase diagrams[1] for the ethyl alcohol-THF-water systems are shown, in which the dissolution temperature is plotted against the sum of the mole fractions, $X=X_{\mathrm{THF}}+X_{\mathrm{alc}}$, where X_{THF}, and X_{alc} are the mole fractions of THF and ethyl alcohol, respectively. Each curve corresponds to the system in which the ratio $X_{\mathrm{THF}}:X_{\mathrm{alc}}$ is kept constant. The curve marked 1:0 is for the THF-water binary system and the congruent melting point at 5.1 °C and X=0.056 indicates the formation of the clathrate hydrate of THF (Type II). Similarly the curve marked 0:1 is for the ethyl alcohol-water binary system. This curve indicates no formation of a clathrate hydrate in the temperature range examined in agreement with several other experiments.[3–5] However, the other two curves (marked with 1:1 and 1:3) in Fig. 1 give no information about the composition of the solid phase since, in these ternary systems, the abscissa of Fig. 1 does not indicate a solid phase composition even at a peak position.[1] A direct determination of the composition of the solid phase is the object of this study as mentioned above. Preliminary experiments showed that, (1) for the systems containing ethyl alcohol with $X_{\mathrm{THF}}+X_{\mathrm{alc}}=0.056$ and $X_{\mathrm{THF}}:X_{\mathrm{alc}}=1:1—1:3$, solid phases formed at temperatures higher than −10 °C were morphologically different from those formed below −10 °C and the latter were identified with ice, and (2) the solid formed from the mixture containing much ethyl alcohol than $X_{\mathrm{THF}}:X_{\mathrm{alc}}=1:4$ was found to be ice. Systems containing methyl alcohol also showed similar behavior except that the limit of the ratio $X_{\mathrm{THF}}:X_{\mathrm{alc}}$ was 1:6 instead of 1:4. From these facts, appropriate experimental conditions were determined as follows: temperature=−6 °C, the molar ratio $X_{\mathrm{THF}}:X_{\mathrm{alc}}=1:1—1:3$ for ethyl alcohol and

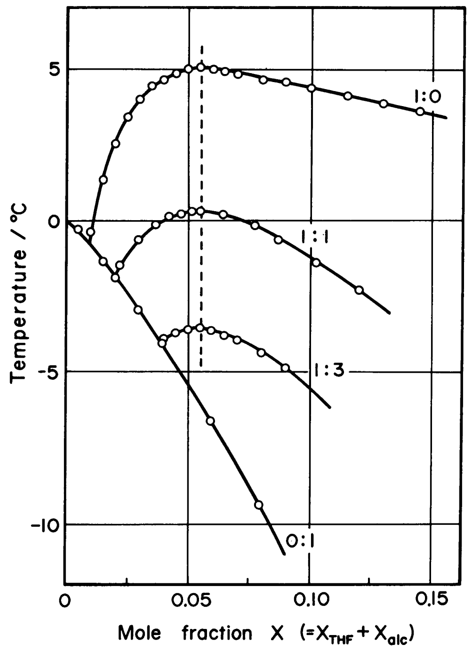

Fig. 1. The solid-liquid phase diagrams for THF–ethyl alcohol–water systems. Explanations are given in the text.

1:0.5—1:4 for methyl alcohol. The mole fraction X was kept constant at 0.056 in all cases.

Results and Discussion

Estimation of the Amount of the Liquid Phase Adhering to the Solid Phase. In order to know the composition of the solid phase exactly, we must first estimate the weight fraction, y, of the liquid phase coexisting with the wet solid sample separated from a supernatant solution. Since, if alcohol can form a mixed clathrate hydrate with THF expressed by a formula $(\text{alcohol})_x(\text{THF})_{1-x}\cdot 17H_2O$, x should decrease with increasing temperature, as exemplified by other systems,⁶⁾ we tentatively assumed that x was equal to zero for the solid formed at a temperature as high as possible. Based upon this assumption the value of y was estimated to be 0.46 for the systems containing ethyl alcohol from the radioactivity measurements for the solid formed from the mixtures of $X_{\text{THF}}:X_{\text{alc}}=1:1$ at −2.5 °C and −3.7 °C, and 0.35 for the systems containing methyl alcohol from the data corresponding to $X_{\text{THF}}:X_{\text{alc}}=1:0.5$ at −0.5 °C. We further assumed that the same y values could be used in analyzing the experimental results since (1) the appearance of the solid phase (formed at −6 °C) was closely the same as when values above y were estimated, and (2) the temperature dependence of y was proved to be negligible.

Enclathration of Alcohols within the Water Lattice of the Clathrate Hydrate of THF. Using the y values evaluated above, the observed x's in an assumed formula $(\text{alcohol})_x(\text{THF})_{1-x}\cdot 17H_2O$ are summarized in Table 1. Each value is an average of 5—10 measurements.

Table 1 shows that x's for the systems containing ethyl alcohol are relatively small, around 0.05, and almost constant irrespective of the molar ratio $X_{\text{THF}}:X_{\text{alc}}$, indicating that ethyl alcohol can be enclathrated within the lattice of the THF clathrate hydrate from the following reasons: (1) if ethyl alcohol cannot form a mixed clathrate hydrate with THF, x should likewise be zero as assumed in the estimation of y; and (2) a solid-liquid phase diagram of the system which forms a mixed clathrate hydrate requires that x should be constant at a given temperature regardless of the composition of the system,⁶⁾ in fair agreement with the above experimental results.

Table 1. The observed x values in the assumed formula $(\text{alcohol})_x(\text{THF})_{1-x}\cdot 17H_2O$ for the solid formed at −6 °C in ternary mixtures of alcohol-THF-water with $X_{\text{THF}}+X_{\text{alc}}=0.056$

Alcohol	$X_{\text{THF}}:X_{\text{alc}}$	x
Ethyl alcohol	1 : 2	0.055
	1 : 3	0.044
Methyl alcohol	1 : 2	0.024
	1 : 3	0.16
	1 : 4	0.29

It can also be concluded that methyl alcohol is included within the THF clathrate hydrate lattice since the x values in Table 1 are larger than zero. However, in contrast to the systems containing ethyl alcohol, x increases with increasing methyl alcohol content. Although a precise explanation for this phenomenon cannot be given because of the lack of any other information, one possibility would be that methyl alcohol can also be accommodated within such vacant water cages as 12-hedron or 14-hedron as well as 16-hedron as its concentration increases. This phenomenon will be, in a sense, a typical one for an inclusion compound as exemplified by the fact that, in a gas hydrate, the degree of occupancy of a guest molecule increases with increasing its partial pressure.

References

1) H. Nakayama and M. Hashimoto, *Bull. Chem. Soc. Jpn.*, **53**, 2427 (1980).

2) D. W. Davidson, S. R. Gough, J. A. Ripmeester, and H. Nakayama, *Can. J. Chem.*, **59**, 2587 (1981).

3) A. D. Potts and D. W. Davidson, *J. Phys. Chem.*, **69**, 996 (1965).

4) P. Boutron and A. Kaufmann, *J. Chem. Phys.*, **68**, 5032 (1978).

5) J. B. Ott, J. R. Goates, and B. A. Waite, *J. Chem. Thermodyn.* **11**, 739 (1979).

6) H. Nakayama, M. Asano, Y. Nakajima, and K. Hanno, *Nippon Kagaku Kaishi*, **1983**, 269.