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Hydrates of Organic Compounds. XII. Intercalation of Methyl and Ethyl Alcohols within the Clathrate-Like Hydrates of Tetrabutylammonium Fluoride and of Tetrabutylammonium Propionate

Haruo NAKAYAMA,* Kiyoshi TSUNAKAWA, Mizue KANŌ, and Hiroshi MATSUI†
Department of Chemistry, Faculty of Engineering, Yokohama National University,
Tokiwadai, Hodogaya-ku, Yokohama 240
†The Radio Isotope Center, Yokohama National University,
Tokiwadai, Hodogaya-ku, Yokohama 240

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The amount of either methyl or ethyl alcohol intercalated within clathrate-like hydrates of tetrabutylammonium fluoride and of tetrabutylammonium propionate has been determined using ^{14}C-labeled alcohols. It was found that (1) methyl alcohol could be intercalated within the tetrabutylammonium fluoride hydrate but not within the tetrabutylammonium propionate hydrate; (2) ethyl alcohol could be intercalated within both the tetrabutylammonium fluoride and tetrabutylammonium propionate hydrates; and (3) the amount of the alcohol intercalated increased with increasing concentration of alcohol in the initial solutions. These results were interpreted by taking into consideration the states of vacant pentagonal dodecahedra formed by hydrogen-bonded water networks.

As a way of examining the ability of an organic substance to form a clathrate-like hydrate, we have proposed a new method.[1,2] It is based upon the examination of the formation of either double or mixed hydrates in a ternary system consisting of the substance under consideration, water, and a third component which is clearly known to form a clathrate-like hydrate by itself. In an earlier experiment[2] for ternary systems of methyl (or ethyl) alcohol–water–tetrahydrofuran(THF), it was found that (1) both methyl and ethyl alcohols were intercalated within the THF clathrate hydrate, (2) ethyl alcohol could form a mixed hydrate with THF, and (3) the amount of methyl alcohol intercalated within the THF hydrate increased with increasing the concentration of methyl alcohol, indicating that methyl alcohol formed a double hydrate with THF, presumably by being intercalated in a vacant pentagonal dodecahedron. These results suggest that the state of vacant polyhedra, especially of vacant pentagonal dodecahedra, plays an important role for the intercalation of such alcohols into a clathrate-like hydrate.

On the other hand, according to the single-crystal X-ray examination for a clathrate-like hydrate of tetrabutylammonium fluoride, $(n\text{-}C_4H_9)_4NF$, by Jeffrey et al.,[3] vacant pentagonal dodecahedra coexist with large polyhedra (such as tetrakaidecahedra and pentakaidecahedra) which accommodate one of the butyl groups of a tetrabutylammonium cation, and five pentagonal dodecahedra face-share with each other and form a part of anionic host structure together with the fluoride ions. It is of interest to examine the capability of these pentagonal dodecahedra to intercalate such small organic molecules as methyl and ethyl alcohols.

Furthermore, it has recently been known that various tetrabutylammonium carboxylates, $(n\text{-}C_4H_9)_4NOOCC_2H_5$ for example, can also form a clathrate-like hydrate having the same hydration numbers as that of the tetrabutylammonium fluoride hydrate (around 30).[4–6] It has been presumed that (1) these carboxylate hydrates are iso-structural with the $(n\text{-}C_4H_9)_4NF$ hydrate and (2) an alkyl group of the carboxylate anion occupies one pentagonal dodecahedron which is located in the nearest position to the tetrabutylammonium cation. If this speculation is correct, there may be some difference in the states of the pentagonal dodecahedra between the $(n\text{-}C_4H_9)_4NF$ hydrate and the tetrabutylammonium carboxylate hydrates, i.e., all the pentagonal dodecahedra are vacant in the former, whereas some of them are already occupied by the alkyl group of the carboxylate anion in the latter.

In this investigation, the enclathration of methyl and ethyl alcohols within the clathrate-like hydrates of $(n\text{-}C_4H_9)_4NF$ and $(n\text{-}C_4H_9)_4NOOCC_2H_5$ has been investigated in order to see if (1) such alcohols can actually be intercalated in vacant pentagonal dodecahedra existing in these tetrabutylammonium salt hydrates and (2) there exists some difference in the intercalation abilities between the two hydrates.

Experimental

Materials and Procedure. An aqueous solution of tetrabutylammonium fluoride was prepared by neutralization of an aqueous solution of tetrabutylammonium hydroxide with hydrofluoric acid. The hydroxide solution was prepared by reacting tetrabutylammonium iodide, which was prepared and purified by the same procedure as in earlier papers,[4,5] with freshly prepared silver hydroxide in water, followed by filtration of the silver iodide precipitate. An aqueous solution of tetrabutylammonium propionate was prepared by reacting the tetrabutylammonium iodide with silver propionate in water, followed by filtration of the silver iodide precipitate. The silver propionate was prepared by reacting sodium propionate with silver nitrate in water, followed by repeated washing with water to remove sodium nitrate. The concentration of the mother solutions of the tetrabutylammonium salts was determined by titration with tetraphenylborate aqueous solution standardized by pure tetrabutylammonium iodide. Radioactive methyl and ethyl alcohols were purchased from The Japan Radioisotope Association. Sample solutions were prepared by dissolving a known amount (0.2—1.0 g) of the sample containing 0.1—0.3 μCi in 4—5 cm^3 of scintillator, Insta-gel (Packard Instrument Co., Inc.). The radioactivity was measured using the TRI-CARB 460C Automatic Liquid Scintillation System (Packard Instrument Co., Inc.).

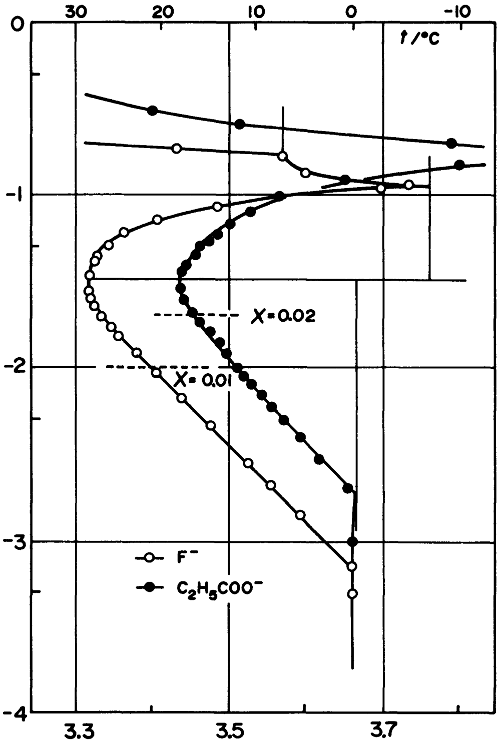

Fig. 1. The solid-liquid phase diagrams for the binary systems of $(n\text{-}C_4H_9)_4NF+H_2O$(○) and $(n\text{-}C_4H_9)_4NOOCC_2H_5+H_2O$(●). The mole fraction ($X$) which is kept constant throughout this study is shown for each salt.

Determination of the Experimental Conditions. In Fig. 1, the solid-liquid phase diagrams for the binary systems of $(n\text{-}C_4H_9)_4NF\text{-}H_2O$[7] and of $(n\text{-}C_4H_9)_4NOOCC_2H_5\text{-}H_2O$[4] are shown, in which the ordinate represents the logarithm of the concentration expressed by the mole fraction (X) of each salt and abscissa represents the reciprocal of the absolute temperature. These phase diagrams clearly indicate the formation of hydrates for both salts. The congruent composition of the hydrate is around X=0.032 for both hydrates and the congruent melting point is 28.3 °C[7] for the fluoride hydrate and 18.0 °C[4] for the propionate hydrate, respectively. As is obvious from this figure, the experimental temperature range is inevitably limited between the eutectic point (around 0 °C for both hydrates) and the congruent melting point of the hydrate, and is highly dependent upon the concentration of each tetrabutylammonium salt. Therefore, the concentration of the tetrabutylammonium salt, which is kept constant throughout this experiment, is determined to be X=0.01 for the systems containing the $(n\text{-}C_4H_9)_4NF$ and X=0.02 for those containing the $(n\text{-}C_4H_9)_4NOOCC_2H_5$, respectively. This situation is also depicted in Fig. 1.

In Fig. 2 the melting points of the two hydrates are plotted against the concentration of the alcohol added. These data were obtained by the usual ampoule method used in

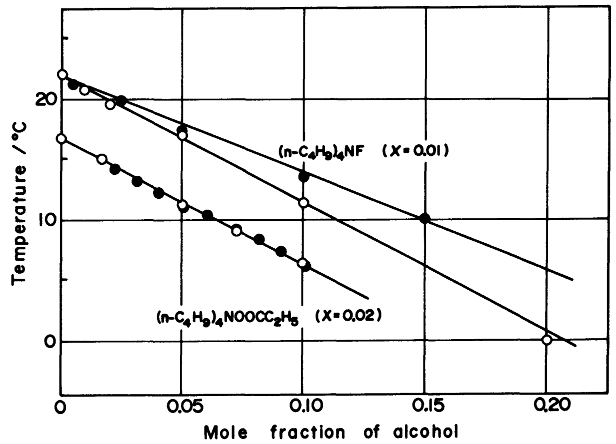

Fig. 2. The effect of added alcohols on the melting points of the clathrate-like hydrates of $(n\text{-}C_4H_9)_4NF$ and of $(n\text{-}C_4H_9)_4NOOCC_2H_5$. The mole fraction of each salt is kept constant at the value given in parenthesis. ○: CH_3OH; ●: C_2H_5OH.

Table 1. List of the Experimental Conditions

No.	Tetrabutylammonium salt	Alcohol	X_{TBA}	X_{alc}	Experimental temperature/°C
1	$(n\text{-}C_4H_9)_4NF$	CH_3OH	0.01	0.01	15.0
2	$(n\text{-}C_4H_9)_4NF$	CH_3OH	0.01	0.10	5.0
3	$(n\text{-}C_4H_9)_4NF$	C_2H_5OH	0.01	0.01	17.5
4	$(n\text{-}C_4H_9)_4NF$	C_2H_5OH	0.01	0.10	9.5
5	$(n\text{-}C_4H_9)_4NOOCC_2H_5$	CH_3OH	0.02	0.02	12.0
6	$(n\text{-}C_4H_9)_4NOOCC_2H_5$	CH_3OH	0.02	0.10	3.1
7	$(n\text{-}C_4H_9)_4NOOCC_2H_5$	C_2H_5OH	0.02	0.02	12.5
8	$(n\text{-}C_4H_9)_4NOOCC_2H_5$	C_2H_5OH	0.02	0.10	3.2

previous papers.[4,5,7] The concentration of the tetrabutylammonium salts are kept constant as mentioned above. This figure indicates that the melting point of each hydrate is lowered almost linearly with increasing concentration of the alcohol. At temperatures above each line only a single liquid phase is present and at temperatures several degrees below the line the mixture apparently looks like a single solid phase in which the coexisting liquid phase is absorbed in the interstice between the hydrate crystal. Therefore, the experimental temperature at which both liquid and solid phases are present in nearly equal proportion is limited to a temperature of a few degrees below each line.

From these standpoints all the experimental conditions are determined. They are summarized in Table 1. The X_{TBA} and X_{alc} represent the mole fraction of tetrabutylammonium salt and of alcohol added, respectively.

Results and Discussion

(1) Estimation of the Amount of the Liquid Phase Adhering to the Solid Phase. Prior to the main experiment, the weight fraction, P, of the liquid phase adhering to the wet solid phase must be estimated. The process for estimating the P is divided into the following processes: (1) a ternary mixture (about 5 cm^3) containing a given amount of tetrabutylammonium salt, of nonradioactive alcohol, and of water was cooled down to about −20 °C in order to deposit a solid phase, then a large portion of the solid was dissolved by gradual warming to a temperature about one degree above the experimental temperature; (2) a well-formed crystalline phase is slowly developed by cooling again to the experimental temperature listed in Table 1; (3) a small amount of radioactive alcohol (0.1—0.3 μCi) is added into the solid-liquid mixture which is kept at the experimental temperature and well mixed with the liquid phase by shaking; and (4) the liquid phase is separated from the solid phase by decantation, followed by suction through a long thin syringe needle. The radioactivity per unit weight is then measured for the liquid phase and for the solid phase, respectively.

If we represent the radioactivity (dpm) and the weight (g) of the sample by r and m, and the liquid phase by a suffix l and the wet solid phase by s, P can be calculated by the following equation:

$$P = \frac{r_s/m_s}{r_l/m_l}, \tag{1}$$

since the amount of the liquid phase contained in the m_s g wet solid is equal to the quantity $(m_l/r_l)r_s$. In this procedure, it is assumed that radioactive alcohol is not present in the solid phase since additional solid phase deposition owing to the addition of alcohol is impossible: i.e., the addition of alcohol never causes the rise in the melting point as shown in Fig. 2 and the temperature is always kept constant. The P values of all the systems determined by this procedure are summarized in Table 2. The number of the system is the same as that listed in Table 1. These values are averages of 5—10 measurements and the limits of error attached to each value simply represent the deviation from the mean value from experiment to experiment. In general, a long and well-shaped, parallelepiped crystal was formed in the systems 1 to 4, especially in the systems containing ethyl alcohol, leading to small values of P. However, in the systems containing $(n\text{-}C_4H_9)_4NOOCC_2H_5$ (systems 5—8), many thin and wedge-shaped crystals were developed almost simultaneously over the whole part of the solution, resulting in relatively large and less accurate values of P.

Table 2. Summary of P Values for All the Systems Examined

System[a)]	P	System[a)]	P
1	0.097±0.006	5	0.09±0.04
2	0.097±0.005	6	0.29±0.06
3	0.017±0.010	7	0.24±0.03
4	0.040±0.009	8	0.12±0.03

a) The number of the system stands for the same one listed in Table 1.

(2) Enclathration of Alcohols within the Clathrate-Like Hydrates of Tetrabutylammonium Fluoride and of Tetrabutylammonium Propionate. Through the measurements of radioactivity of ^{14}C-labeled alcohols, the amount of either methyl or ethyl alcohol included in the hydrate solid which is formed in ternary mixtures of tetrabutylammonium fluoride (or propionate)–radioactive methyl (or ethyl) alcohol–water has been determined. The solid phase was carefully developed by the same procedure as the processes (1) and (2) described in the preceding section.

Since water networks which have the possibility to enclathrate alcohol molecules are vacant pentagonal dodecahedra, the molar ratio of the tetrabutylammonium salt to water in the hydrate solid remains unchanged, i.e., 1:30, irrespective of the presence of alcohol within the hydrate solid. Therefore, the molecular formula of the solid phase may be expressed as (Tetrabutylammonium salt)(Alcohol)$_x$30H$_2$O. The maximal value of x is equal to 2 according to the crystal structure examination by Jeffrey et al.[3] Thus, the following relation can be obtained with respect to the amount of alcohol existing in the solid phase:

$$\frac{M_{\mathrm{alc}}x}{M_{\mathrm{TBA}}+M_{\mathrm{alc}}x+30M_{\mathrm{H_2O}}} = \frac{w_s-Pw_l}{1-P}, \tag{2}$$

in which M_{TBA}, M_{alc}, and $M_{\mathrm{H_2O}}$ are the molecular weights of tetrabutylammonium salt, alcohol, and water, and w_s and w_l, are the weight fractions of the alcohol in the wet solid phase and in the liquid phase, respectively. These two weight fractions were

Table 3. The x Values Determined for All the Systems Examined

System[a)]	x	System[a)]	x
1	0.12±0.03	5	0.03±0.03
2	0.71±0.10	6	0.21±0.25
3	0.10±0.01	7	0.12±0.05
4	0.75±0.10	8	0.79±0.10

a) The number of systems is the same as listed in Table 1.

determined by the radioactivity measurements for both phases separated from each other by the same procedure as the process (4) in the previous section. From Eq. 2 we can get the following relation:

$$x = \frac{w_s - Pw_l}{1 - P - (w_s - Pw_l)} \cdot A, \tag{3}$$

where A is a constant calculated from the molecular weight of each component in ternary mixtures: A is equal to 25.03 for systems 1 and 2; 17.41 for systems 3 and 4; 26.72 for systems 5 and 6; and 18.58 for systems 7 and 8.

The values of x determined for all the systems are summarized in Table 3. These values are averages of 5—10 measurements. The limit of error attached to each x is estimated by taking into consideration the uncertainty of the P values (Table 2) and the error arising from the radioactivity measurements. In system 6 the deviation from the mean value is exceptionally large because of the difficulty to obtain a well-formed crystal in this system as partly exemplified by large P value for this system (Table 2).

From these results the following conclusions can be drawn:

(1) In the systems containing tetrabutylammonium fluoride (systems 1—4), both methyl and ethyl alcohols are intercalated within the hydrate solid.

(2) In the systems 1—4, the amounts of alcohol intercalated increase with increasing concentration of alcohol in the initial solutions, showing a feature characteristic of a nonstoichiometric inclusion compound. The increment of x is 5.9 times for methyl alcohol and 7.5 times for ethyl alcohol for the 10 times increment of the mole fraction of each alcohol, i.e., from X=0.01 to 0.10.

(3) For the systems 5 and 6, taking into account the relatively small values of x and the deviations from the mean values, it may be concluded that methyl alcohol is not intercalated within the tetrabutylammonium propionate hydrate.

(4) On the other hand, the values of x for the systems 7 and 8 clearly indicate that ethyl alcohol is intercalated within the tetrabutylammonium propionate hydrate. The values of x for the systems 7 and 8 are similar to those of the systems 3 and 4, respectively.

As mentioned in the introduction section, in the structure of the tetrabutylammonium fluoride hydrate[3)] there exists a vacant space which is made of five pentagonal dodecahedra face-sharing with each other. However, this space must be appreciably deformed by the arrangement of other large polyhedra like tetrakaidecahedra and pentakaidecahedra which accommodate butyl groups of a tetrabutylammonium cation. The experimental above listed facts may be explained if we assume the presence of at least two types of pentagonal dodecahedra, i.e., geometrically highly deformed pentagonal dodecahedra which exist near the tetrabutylammonium cation (denoted by S-type hereafter) and geometrically less deformed ones which exist somewhat apart from the tetrabutylammonium cation (denoted by L-type hereafter).

Taking into account the fact that free diameter of a nondeformed pentagonal dodecahedron is about 5.2 Å[8)] and the molecular diameter of methyl alcohol is about 5.2 Å and that of ethyl alcohol is about 6.3 Å, it will be reasonable to assume that methyl alcohol is enclathrated in the S-type pentagonal dodecahedra and ethyl alcohol in the L-type ones. This assumption means that the free diameter of the L-type pentagonal dodecahedron is elongated enough to accommodate an ethyl alcohol molecule. These assumptions lead to a conclusion compatible with the experimental facts: (1) since in the $(n\text{-}C_4H_9)_4NF$ hydrate the S-type pentagonal dodecahedron is vacant, it can enclathrate methyl alcohol; (2) however, the S-type pentagonal dodecahedron in the $(n\text{-}C_4H_9)_4NOOCC_2H_5$ hydrate must accommodate the C_2H_5 group of the $C_2H_5COO^-$ ion, it can enclathrate methyl alcohol no longer; and (3) since the L-type pentagonal dodecahedra are considered to be in a similar situation in both hydrates, their ability to enclathrate ethyl alcohol is expected to be similar in both hydrates.

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