Hydrates of Organic Compounds. II. The Effect of Alkyl Groups on the Formation of Quaternary Ammonium Fluoride Hydrates

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The solid–liquid phase diagrams for the binary mixtures of water with various quaternary ammonium fluorides, $(n\text{-}C_4H_9)_3RNF$ (R=H, CH_3, C_2H_5, $n\text{-}C_3H_7$, $i\text{-}C_3H_7$, $n\text{-}C_4H_9$, $i\text{-}C_4H_9$, $n\text{-}C_5H_{11}$, $i\text{-}C_5H_{11}$, $n\text{-}C_6H_{13}$, $n\text{-}C_7H_{15}$, and $C_6H_5CH_2$), have been determined in order to see the effect of alkyl groups on the formation of clathrate hydrates. It has been found that, among these compounds, not only $(n\text{-}C_4H_9)_4NF$, which has been known as a clathrate hydrate-forming salt, but also several other compounds with R=C_2H_5, $n\text{-}C_3H_7$, $i\text{-}C_3H_7$, $i\text{-}C_4H_9$, $n\text{-}C_5H_{11}$, and $i\text{-}C_5H_{11}$ can form hydrate type. These hydrates are believed to be of the clathrate hydrates since they have almost the same hydration numbers as that of $(n\text{-}C_4H_9)_4NF$ hydrate. From the melting points of these hydrates, it has been concluded that the most suitable alkyl chain length of quaternary ammonium salts for their clathrate-hydrate formation is C_4-chain (butyl or isopentyl). In the cases of R=CH_3 and $C_6H_5CH_2$, hydrates having lower melting points and smaller hydration numbers than those of the above group of hydrates have been detected. No hydrates have been observed for the salts with R=H, $n\text{-}C_6H_{13}$ and $n\text{-}C_7H_{15}$.

In 1940 the formation of a variety of crystalline hydrates of tetra butyl and tetra isopentyl quaternary ammonium salts was reported by Kraus and his coworkers.[1] Later McMullan and Jeffrey[2-4] carried out a detailed X-ray structural analysis of the hydrates formed by a large number of these salts and have found that they were the clathrate type, similar to the gas hydrates.[5] In these hydrates, the central N^+ atom lies at a common vertex of four large polyhedra formed by the association of water molecules through hydrogen bondings, and each of the four alkyl chains extends into one of the polyhedral cages. Up to the present it has been known that these hydrates have various characteristic features: 1) an unusually high proportion of water of crystallization; 2) high melting points as compared with ordinary gas hydrates; 3) the capability of forming hydrates with various kinds of anions. However, so far as we know, no systematic investigation of these properties, particularly of their thermodynamic properties, such as heats of fusion of the hydrates and vapor pressure of water molecules which form polyhedral cages, has been extensively done. There is no doubt that such information would be very helpful for the studies of aqueous solutions of these compounds, particularly in connection with the structural modification of water molecules in the vicinity of hydrophobic solutes.[6]

First of all, we are here concerned mainly with the effect of alkyl chain length and/or shape on the stability of the clathrate hydrates of quaternary ammonium salts. It has been reported that quaternary ammonium salts having either a butyl or an isopentyl group can make fairly stable crystalline hydrates. On the other hand an attempt to make the hydrates of tetra propyl ammonium salts was unsuccessful.[7] We have examined as well the solid–liquid phase diagram of the system $(n\text{-}C_3H_7)_4NF$+water and concluded that $(n\text{-}C_3H_7)_4NF$ certainly does not form a clathrate hydrate; the phase diagram of this system is shown in Fig. 1. These facts indicate that the stability of the clathrate hydrate of a quaternary ammonium salt depends significantly on the type of its alkyl group.

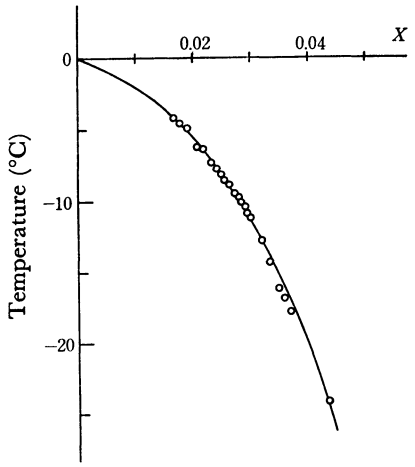

Fig. 1. The solid–liquid phase diagram for the $(n\text{-}C_3H_7)_4NF$+water system; X is the mole fraction of $(n\text{-}C_3H_7)_4NF$.

In order to make this point clearer and, at the same time, to determine what conditions are required for this type of hydrate to be formed (with respect to the length and/or shape of alkyl groups of quaternary ammonium cations), we have examined the formation of hydrates of quaternary ammonium fluorides in which one of the four butyl chains of tetra butylammonium fluoride is substituted for by various kinds of alkyl chains R, *i.e.*, $(n\text{-}C_4H_9)_3RNF$.

Experimental

Alkyltributylammonium iodides (or bromides), $(n\text{-}C_4H_9)_3RNI$ (or Br), were prepared by the quaterization of tributylamine with the appropriate alkyl iodide (or bromide): HI; CH_3I; C_2H_5I; $n\text{-}C_3H_7I$; $i\text{-}C_3H_7I$; $n\text{-}C_4H_9I$; $i\text{-}C_4H_9I$; $n\text{-}C_5H_{11}I$; $i\text{-}C_5H_{11}I$; $n\text{-}C_6H_{13}Br$; $n\text{-}C_7H_{15}Br$; $C_6H_5CH_2Br$. The obtained solid products were recrystallized from ethyl acetate+acetone mixtures and confirmed by the NMR spectra. The aqueous solutions of their fluorides were prepared by the triple decomposition of a mixture of BaF_2, Ag_2SO_4, and the corresponding iodide (or bromide) by using

stoichiometric amounts of the latter two components and an excess of the former.[8] The mixture of the silver salts was removed by filtration.

Each solution (about 5 ml) of a known concentration was sealed in a glass ampoule and was cooled until the solid phase appeared. After being annealed at low temperature for several hours, each ampoule was warmed very slowly in a constant temperature bath with vigorous shaking. By measuring the temperatures, for each ampoule, at which the solid phase disappeared completely, the solid-liquid phase diagram was determined. The differential scanning calorimeter[6] was also employed when the determination of the dissolution temperature was somewhat ambiguous. The water content of each solution was determined by the Karl Fischer titration method.

Results and Discussion

The solid-liquid phase diagrams for the systems water+$(n\text{-}C_4H_9)_3RNF$ with R=H—$n\text{-}C_4H_9$ are shown in Fig. 2, those for the systems water+$(n\text{-}C_4H_9)_3RNF$ with R=$n\text{-}C_5H_{11}$—$n\text{-}C_7H_{15}$, and $C_6H_5CH_2$ are shown in Fig. 3, and those for the systems water+$(n\text{-}C_4H_9)_3$-RNF, with R a branched alkyl group ranging from isopropyl to isopentyl, are shown in Fig. 4. For comparison, the curve for the system water+$(n\text{-}C_4H_9)_4NF$ is also included in Figs. 3 and 4.

As is obvious from these figures, among this series of compounds, the salt $(n\text{-}C_4H_9)_4NF$ forms a hydrate which has the highest melting point, *i.e.*, the most stable hydrate. The melting point and hydration number of this hydrate have been determined to be 28.3 °C and 28.0 (34.1 wt %) respectively. These values are somewhat different from those reported by McMullan and Jeffrey, who reported 24.9±0.1 °C[8] for the melting point and for hydration number 34.0[8] by chemical analysis and 32.8[4] by crystallographic analysis. It is

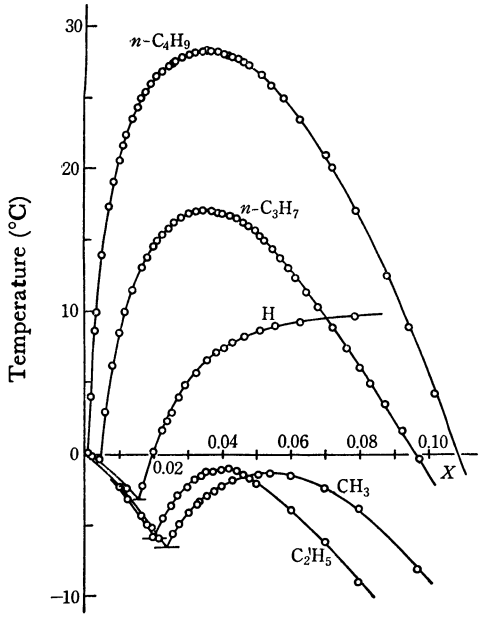

Fig. 2. The solid-liquid phase diagrams for the $(n\text{-}C_4N_9)_3RNF$+water systems; R=H, CH_3, C_2H_5, $n\text{-}C_3H_7$, and $n\text{-}C_4H_9$. X is the mole fraction of the salts.

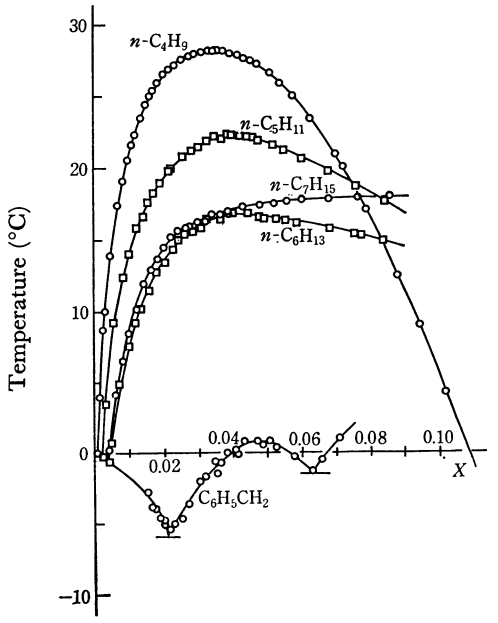

Fig. 3. The solid-liquid phase diagrams for the $(n\text{-}C_4H_9)_3RNF$+water systems; R=$n\text{-}C_4H_9$, $n\text{-}C_5H_{11}$, $n\text{-}C_6H_{13}$, $n\text{-}C_7H_{15}$ and $C_6H_5CH_2$. X is the mole fraction of the salts.

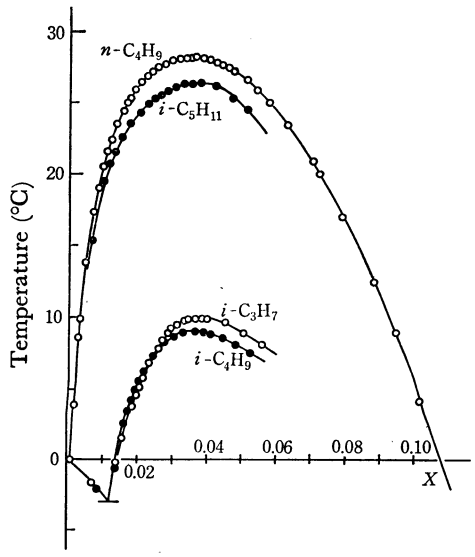

Fig. 4. The solid-liquid phase diagrams for the $(n\text{-}C_4H_9)_3RNF$+water systems; R=$i\text{-}C_3H_7$, $i\text{-}C_4H_9$, $i\text{-}C_5H_{11}$, and $n\text{-}C_4H_9$. X is the mole fraction of the salts.

conceivable that these discrepancies can be attributed to the fact that our values are for the hydrate which is in equilibrium with an aqueous solution of the same composition as that of the hydrate itself. It has been noticed that the composition of the hydrate which is separated from its solution phase and is exposed to the atmosphere varies considerably with time and as a result of this its apparent melting point decreases. Such a property and some other thermodynamic properties of the $(n\text{-}C_4H_9)_4NF$ hydrate are now in under investigation and the results will be published in the near future.

TABLE 1. MELTING POINTS AND HYDRATION NUMBERS OF THE HYDRATES OF TRIBUTYL MONOALKYL AMMONIUM FLUORIDES, $(n\text{-}C_4H_9)_3RNF$

R	Melting point (°C)	Hydration number
CH_3	−1.5	17.5[a)]
C_2H_5	−1.1	26.0
$n\text{-}C_3H_7$	17.1	27.1
$i\text{-}C_3H_7$	10.0	27.6
$n\text{-}C_4H_9$	28.3(24.9[6)])	28.0(32.8[4)]; 34.0[6)])
$i\text{-}C_4H_9$	9.1	28.0
$n\text{-}C_5H_{11}$	22.1	25.4
$i\text{-}C_5H_{11}$	26.4	27.8(32.8[7)])
$C_6H_5CH_2$	1.0	21.5[a)]

a) See text.

Figures 2—4 indicate that $(n\text{-}C_4H_9)_3(C_2H_5)NF$, $(n\text{-}C_4H_9)_3(n\text{-}C_3H_7)NF$, $(n\text{-}C_4H_9)_3(i\text{-}C_3H_7)NF$, $(n\text{-}C_4H_9)_3(i\text{-}C_4H_9)NF$, $(n\text{-}C_4H_9)_3(n\text{-}C_5H_{11})NF$, and $(n\text{-}C_4H_9)_3(i\text{-}C_5H_{11})NF$ can also make hydrates. The melting points and hydration numbers of these hydrates are summarized in Table 1, together with the values reported before. These hydrates are considered to be of the clathrate type since they have hydration numbers similar to that of the $(n\text{-}C_4H_9)_4NF$ hydrate. This indicates the fact that a formation of a clathrate hydrate of quaternary ammonium salts is not limited only to salts containing either butyl or isopentyl chains, though the melting point is very much affected by a change in length and/or shape of the alkyl chain. The formation of the clathrate hydrate of $(n\text{-}C_4H_9)_3(i\text{-}C_5H_{11})NF$ has been known.[7)] However, as in the case of $(n\text{-}C_4H_9)_4NF$ hydrate, there is some difference in hydration number between our value (27.8) and the reported one (32.8 ± 1).[7)] This discrepancy may also be explained, at least partly, by the same reason as given above in connection with the $(n\text{-}C_4H_9)_4NF$ hydrate.

From Table 1, it can be seen that, for the salts whose R is either a propyl or butyl chain, the hydrate of salt having a normal alkyl chain has a higher melting point than that having a branched alkyl chain; on the contrary, in the hydrates of the salts containing a pentyl group, the isopentyl chain can stabilize the hydrate more effectively than the pentyl chain. These results undoubtedly indicate that the most suitable length of an alkyl chain of quaternary ammonium salt for the formation of a clathrate hydrate is C_4-chain (butyl or isopentyl chain).

The solid-liquid equilibrium curves for the systems of water+$(n\text{-}C_4H_9)_3(CH_3)NF$ and water+$(n\text{-}C_4H_9)_3(C_6H_5CH_2)NF$ (Figs. 2 and 3) suggest a formation of hydrates. However, these hydrates do not seem to belong to the same group as the $(n\text{-}C_4H_9)_4NF$ hydrate since the hydration numbers (Table 1) are rather low as compared with that of the $(n\text{-}C_4H_9)_4NF$ hydrate. For the systems $(n\text{-}C_4H_9)_3HNF$+water, $(n\text{-}C_4H_9)_3(n\text{-}C_6H_{13})NF$+water, and $(n\text{-}C_4H_9)_3(n\text{-}C_7H_{15})NF$+water, the formation of hydrates was not recognized. Although the solid-liquid phase equilibrium curve exhibits a slight maximum in the system of $(n\text{-}C_4H_9)_3(n\text{-}C_6H_{13})NF$+water (Fig. 3), it is dubious whether this is due to the formation of a hydrate, since in the solutions whose concentrations are higher than $X=0.04$ (X is the mole fraction of the salt) the appearance of droplets of an oily substance has been observed. This oily substance was identified as tributylamine by means of its NMR spectrum. The same phenomena was also noted in the $(n\text{-}C_4H_9)_3(n\text{-}C_7H_{15})NF$+water system.

In conclusion, it has been found that there is some permitted limit for the length and/or shape of alkyl groups of quaternary ammonium salts if their clathrate hydrates are to be formed. That is, though it seems clear that the most suitable alkyl-chain length for their clathrate-hydrate formation is C_4-chain (butyl or isopentyl chain), other alkyl groups such as propyl, isopropyl, pentyl, and even ethyl, have some ability to make clathrate hydrates.

References

1) D. L. Fowler, W. V. Loebenstein, D. B. Pall, and C. A. Kraus, *J. Am. Chem. Soc.*, **62**, 1140 (1940).
2) D. Feil and G. A. Jeffrey, *J. Chem. Phys.*, **35**, 1863 (1961).
3) M. Bonamico, R. K. McMullan, and G. A. Jeffrey, *J. Chem. Phys.*, **37**, 2219 (1962).
4) R. K. McMullan, M. Bonamico, and G. A. Jeffrey, *J. Chem. Phys.*, **39**, 3295 (1963).
5) M. von Stackelberg, *Z. Elektrochem.*, **58**, 24 (1954).
6) H. Nakayama and M. Tahara, *Bull. Chem. Soc. Jpn.*, **46**, 2965 (1973).
7) G. Beurskens, G. A. Jeffrey, and R. K. McMullan, *J. Chem. Phys.*, **39**, 3311 (1963).
8) R. K. McMullan and G. A. Jeffrey, *J. Chem. Phys.*, **31**, 1231 (1959).