Hydrates of Organic Compounds. VIII. The Effect of Carboxylate Anions on the Formation of Clathrate Hydrates of Tetrabutylammonium Carboxylates

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The solid-liquid phase diagrams of binary mixtures of tetrabutylammonium carboxylates, $(n\text{-}C_4H_9)_4NOOCR$ ($R=H\text{-}n\text{-}C_{10}H_{21}$ including various alkyl groups replaced by either methyl or ethyl group), with water were examined in order to confirm the formation of clathrate-like hydrates. The results can be summarized as follows: (1) for 14 carboxylates the formation of a clathrate-like hydrate is newly confirmed; (2) judging from melting points and hydration numbers, the hydrates can be classified into three groups: I, II, and III; (3) the group I hydrates, formed by the carboxylates with $R=H$, CH_3, C_2H_5, $n\text{-}C_3H_7$, $i\text{-}C_3H_7$, and $t\text{-}C_4H_9$, have hydration numbers around 30 and are the most stable hydrates among those examined in this experiment, with the exceptions of 2-methylpropionate and 2,2-dimethylpropionate hydrates; (4) the group II hydrates, with hydration numbers around 39, are formed by the salts with $R=n\text{-}C_4H_9$, $s\text{-}C_4H_9$, $i\text{-}C_4H_9$, and all the C_5H_{11}, and are relatively unstable (mp=5—11 °C); (5) the group III hydrates, with hydration numbers around 30 like the group I hydrates, are formed by the carboxylates with long alkyl chains from $n\text{-}C_6H_{13}$ to $n\text{-}C_{10}H_{21}$ and are generally unstable; and (6) judging from the hydration number, the crystal structure of the group I and III hydrates seems to be isomorphous with a tetrabutylammonium fluoride hydrate, and that of the group II hydrates with a tetrabutylammonium benzoate hydrate.

As early as 1940, the formation of unusual hydrates of tetrabutylammonium carboxylates like formate and benzoate, which had a large number of water molecules per one salt molecule, was reported by Kraus *et al.*[1)] In the subsequent crystallographic studies made by Jeffrey and his coworkers, it was concluded that hydrates of tetrabutylammonium acetate[2)] and of tetrabutylammonium benzoate[3)] had a clathrate-like structure similar in general character to the gas hydrates: the structure of the acetate hydrate is isomorphous with tetrabutylammonium fluoride hydrate,[4)] in which each butyl group of the ammonium cation is located in a hydrogen-bonded framework of water molecules; and in the tetragonal benzoate hydrate, not only four butyl groups of the cation but also one benzyl group of the anion is surrounded by a hydrogen-bonded water framework.

Thus, there are at least two types of tetrabutylammonium carboxylate hydrates. However, we have no sufficient data to draw any conclusion as to the influence of an alkyl chain of a carboxylate anion on both the stability and the structure of the tetrabutylammonium carboxylate hydrates. In this paper, from the solid-liquid phase diagrams for 19 binary mixtures of tetrabutylammonium carboxylate-water, the effect of the shape and/or length of the alkyl group of a carboxylate anion on the stability (*i.e.*, melting point) and the crystal structure (*i.e.*, hydration number) of their clathrate hydrates has been systematically examined. These fundamental data would also offer a guiding principle, for example, for highly selective separation of a specific carboxylate anion from an aqueous solution containing several kinds of carboxylate anions by means of the formation of a mixed clathlate hydrate of tetrabutylammonium carboxylates.[5)]

Experimental

Aqueous solutions of tetrabutylammonium carboxylates, except for formate, were prepared by a reaction between tetrabutylammonium iodide and the corresponding silver carboxyates in water, followed by filtration of AgI precipiate. Tetrabutylammonium iodide was synthesized by reacting tributylamine with butyl iodide in ethyl acetate and purifie by recrystallization from ethyl acetate-acetone mixture. Each silver carboxylate was obtained by mixing an aqueous solution of silver nitrate with an aqueous carboxylic acid solution after neutralization with NaOH, followed by repeated washing with water in order to remove the resultant sodium nitrate. An aqueous solution of tetrabutylammonium formate was prepared by neutralizing tetrabutylammonium hydroxide solution with formic acid solution. The hydroxide solution was obtained by treating tetrabutylammonium iodide with freshly prepared silver hydroxide in water. The silver hydroxide was obtained by reacting silver nitrate solution with sodium hydroxide solution, followed by filtration and by repeated washing with water. All the carboxylic acids were purchased from Tokyo Kasei Kogyo Co. Ltd. and were used without further purification. Some impurities contained in the carboxylic acid could be removed during the precipitation procedure of the silver salt of the carboxylic acid.

Solid-liquid phase diagrams for the binary systems of water-tetrabutylammonium carboxylate were determined in the same manner as described in the previous paper[6)] (an ampoule method). The concentration of each mother solution was determined by a titration method using a standard sodium tetraphenylborate solution.[6)]

Results and Discussion

The solid-liquid phase diagrams for tetrabutylammonium carboxylate-water binary systems are shown in Figs. 1, 2, and 3. The logarithm of the concentration expressed in mole fraction (X) is plotted against the reciprocal of the absolute temperature. The temperature expressed in ordinary Celsius units is shown on the upper side of each figure. For comparison, Fig. 1 includes the phase diagram of the tetrabutylammonium fluoride-water system reported earlier.[6,7)] Because of the similarity of the data with each other, some of the results

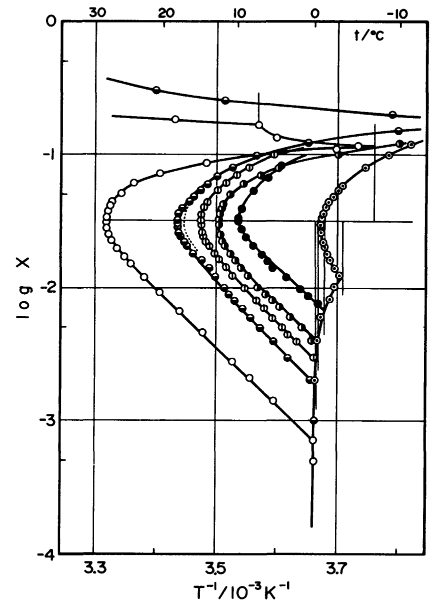

Fig. 1. Solid-liquid phase diagrams for the water-(*n*-$C_4H_9)_4NX$ systems.
○: X=F, ◑: X=HCOO, ⦶: X=CH_3COO, ◒: X=C_2H_5COO, ……: X=*n*-C_3H_7COO, ●: X=*i*-C_3H_7COO, ⊙: X=$(CH_3)_3CCOO$.

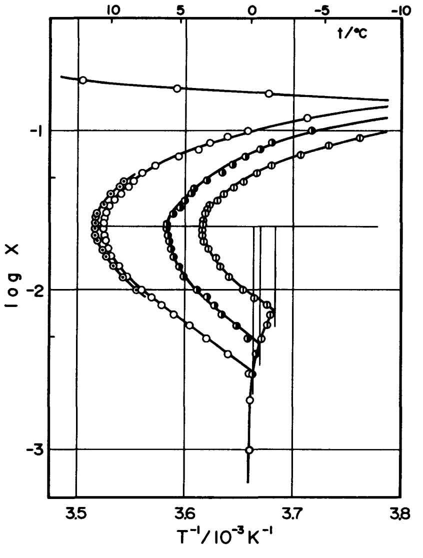

Fig. 2. Solid-liquid phase diagrams for the water-(*n*-$C_4H_9)_4NOOCR$ systems.
○: R=*n*-C_4H_9, ⊙: R=*i*-C_4H_9, ⦶: R=*n*-C_5H_{11}, ◑: R=*i*-C_5H_{11}.

are either excluded from these figures or represented by a dotted or a broken line only in the vicinity of each congruent point. These figures clearly show that all the salts examined in this experiment can form clathrate-like hydrates similar to that of the fluoride, although their congruent melting points are considerably lower than that of the fluoride hydrate (Fig. 1). All the melting points and the hydration numbers, determined from each congruent melting point and congruent composition, are summarized in Table 1, together with those previously reported by other authors.[2,8] Among these hydrates, 14 hydrates which have not been reported earlier are confirmed in this experiment.

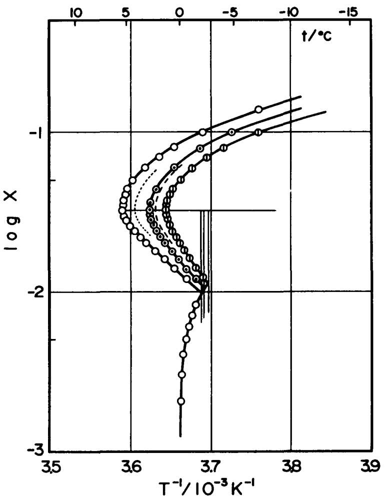

Fig. 3. Solid-liquid phase diagrams for the water-(*n*-$C_4H_9)_4NOOCR$ systems.
----: R=*n*-C_6H_{13}, ⦶: R=*n*-C_7H_{15}, ○: R=*n*-C_8H_{17}, ⊙: R=*n*-C_9H_{19}, ------: R=*n*-$C_{10}H_{21}$.

TABLE 1. MELTING POINTS AND HYDRATION NUMBERS OF THE CLATHRATE HYDRATES FORMED BY A SERIES OF TETRABUTYLAMMONIUM CARBOXYLATES (*n*-$C_4H_9)_4NOOCR$

R	Mp θ_m/°C	Hydration number
H	12.2(11.8[8])	30±1(32[8])
CH_3	14.8(14.9[8]), 15.1[2])	30±1(32[8]), 30.7[2])
C_2H_5	18.0(16.8[8]), 18.1[8])	30±1(32[8])
n-C_3H_7	17.0(15.5[8])	31±1(32[8])
i-C_3H_7	9.8	30±1
n-C_4H_9	10.6(10.2[8])	40±1(40[8])
s-C_4H_9	7.7	40±1
i-C_4H_9	11.3	39±1
t-C_4H_9	−0.7	30±2
n-C_5H_{11}	3.4	40±1
$CH_3(CH_2)_2CH(CH_3)$	5.1	39±2
$CH_3CH_2CH(CH_3)CH_2$	5.1	39±2
$CH_3CH(CH_3)(CH_2)_2$	6.0	39±2
$CH_3CH_2CH(C_2H_5)$	10.6	39±1
n-C_6H_{13}	2.3	30±2
n-C_7H_{15}	1.3	29±2
n-C_8H_{17}	5.4	29±2
n-C_9H_{19}	2.8	31±2
n-$C_{10}H_{21}$	4.3	30±2

In Fig. 4, the melting point of the clathrate hydrate is plotted against the number of carbon atom in the main alkyl chain of each carboxylate anion. The points corresponding to the hydrates of a series of normal alkanoates are connected by a solid line. A filled circle indicates a hydrate with hydration number around 30 and an open circle indicates one with hydration number around 39. From this figure it is clear that the effect of an alkyl chain in the carboxylate anion on the formation of the clathrate hydrate of the tetrabutylammonium carboxylates is fairly complicated and also that all the

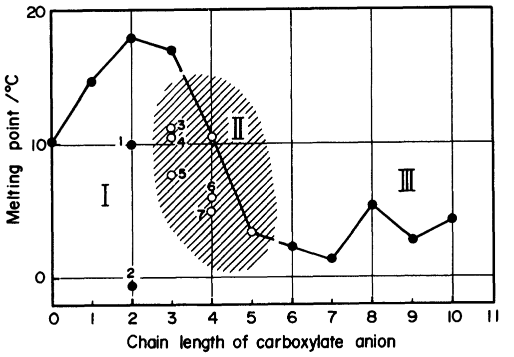

Fig. 4. Relatioship between the melting points of the tetrabutylammonium carboxylate, $(n\text{-}C_4H_9)_4NOOCR$, hydrates and the chain length of R in the carboxylate anion. Filled circle indicates the hydrate with hydration number of 30 and open circle indicates the one with hydration number of 39. All points not numbered indicate that R is normal alkyl group. Numbered point means as follows: 1: $R{=}CH_3CH(CH_3)$; 2: $R{=}(CH_3)_3C$; 3: $R{=}CH_3CH(CH_3)CH_2$; 4: $R{=}CH_3CH_2C(C_2H_5)$; 5: $R{=}CH_3CH_2CH(CH_3)$; 6: $R{=}CH_3CH(CH_3)CH_2CH_2$; 7: $R{=}CH_3(CH_2)_2CH(CH_3)$ and $R{=}CH_3CH_2CH(CH_3)CH_2$. Three groups shown by I, II, and III are explained in the text.

points corresponding to the hydrates of hydration number 39 (open circles) gather in a limited region (shown by the hatched area). Thus, we analyze these results by classifying, tentatively, these hydrates into three groups: I, II, and III, as also indicated in Fig. 4.

The group I hydrates include the hydrates formed by the carboxylates with $R{=}H$, CH_3, C_2H_5, $n\text{-}C_3H_7$, $i\text{-}C_3H_7$, and $t\text{-}C_4H_9$. These hydrates, except for the 2,2-dimethylpropionate hydrate, are fairly stable as compared with hydrates in the other groups. The fact that the hydration number of these hydrates is around 30, just as the fluoride hydrate, suggests that the crystal structue of the group I hydrate is isomorphous with that of the fluoride hydrate.[4] In fact McMullan and Jeffrey[2] have reported that the tetrabutylammonium acetate hydrate forms the same tetragonal crystal as those of such salts as fluoride, chloride, and bromide. Very recently, in the course of our investigation Dyadin *et al.*[8] have also reported that four tetrabutylammonium carboxylates having $HCOO^-$, CH_3COO^-, $C_2H_5COO^-$, and $n\text{-}C_3H_7OO^-$ anion can form a clathrate-like hydrate which is tetragonal and has 32 mol of water per one mole of the salt.

However, the effect of carboxylate anions on the stability of these group I hydrates cannot be explained by the same consideration as that applied to the hydrates of ordinary tetrabutylammonium inorganic salts.[6] In the previous paper,[6] we pointed out that the stability of the ordinary $(n\text{-}C_4H_9)_4NX$ (X = monovalent inorganic anion) hydrates approximately decreased with increasing the ionic volume of the X. This relationship is represented in Fig. 5, in which the melting point of each hydrate is plotted against the conventional partial molal anionic volume ($\bar{V}^\circ_{conv}$) at 25 °C as an indication of the effective volume of an anion within the hydrate solid. This nearly linear relationship between the melting point (*i.e.*, the stability) of the hydrate and $\bar{V}^\circ_{conv}$ of its anion[9] indicates that the stability of the hydrate is mainly governed by the distortion effect of the anion on the hydrogen-bonded water framework in the hydrate. In Fig. 5, similar plots are also given for the group I hydrates. The conventional partial molal volume of each carboxylate anion was obtained from the partial molal volumes of each sodium salt[10—12] at infinite dilution using the relation that $\bar{V}^\circ_{conv}$ for Na^+ is equal to $-1.21\ cm^3/mol$ at 25 °C.[9] As is obvious from this figure, these plots, except for the formate hydrate, appreciably deviate from the simple, linear relationship found for the ordinary inorganic salt hydrate. This indicates that the stability of the group I hydrate, except for the formate hydrate, cannot be explained by a simple distortion effect caused by the presence of the carboxylate anion within the hydrate lattice.

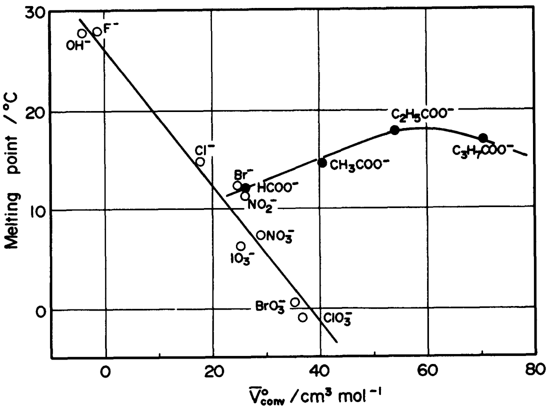

Fig. 5. Relationship between the melting points of the hydrates of tetrabutylammonium salt, $(n\text{-}C_4H_9)_4NX$, and the conventional partial molal ionic volumes of the anion X.

A reasonable explanation for this behavior will be that such alkyl groups as CH_3, C_2H_5, and C_3H_7 are located in a pentagonal dodecahedron, which exists in a gap between the arrangement of larger polyhedra (tetrakaidecahedra and/or pentakaidecahedra filled by one of the butyl group of the tetrabutylammonium cation) and is believed to be either vacant or partially filled by a small molecule such as free water, oxygen, and nitrogen. Very recently, a similar consideration has been proposed by Dyadin *et al.*[8] on the basis of X-ray diffraction characteristics.

Our reasons derived from this investigation are summarized as follows: (1) the occupation of a pentagonal dodecahedron by an akyl group of a carboxylate anion will not cause any change in the crystal structure or the hydration number of the hydrate since the fundamental network of the hydrogen-bonded water molecules has nothing to do with the occupation of a pentagonal dodecahedron; (2) the best fitness of $CH_3CH_2COO^-$ anion to a pentagonal dodecahedron, as revealed by the highest melting point of the propionate hydrate, can be reasonably explained since the mean free diameter of a pentagonal dodecahedron is about 5.0 Å[13] and the van der Waals diameter of $CH_3CH_2COO^-$ anion is estimated to be 4.7Å if we take into account the fact that the oxygen atoms of the carboxylate anion are hydrogen-bonded to the water framework and form part of the polyhedral structure;[3] and (3) low stability of both 2-

methylpropionate and, especially, 2,2-dimethylpropionate hydrates can be interpreted by a distortion of pentagonal dodecahedron due to the presence of these bulky, methyl-substituted anions.

The group II hydrates include all the hydrates with the hydration number of 39. They are formed exclusively by all the carboxylates with R=C_4H_9 and C_5H_{11} except for t-C_4H_9, and are newly confirmed in this experiment except for the pentanoate hydrate.[8] The large hydration number, 39, as compared with that of the group I hydrate, 30, indicates that one more hydrogen-bonded water cage will be present in order to enclathrate such a fairly large carboxylate anion as $C_4H_9COO^-$ or $C_5H_{11}COO^-$, which is too large to be accommodated in a pentagonal dodecahedron just as considered for the group I hydrate. Although there is no more evidence about the crystal structure of the group II hydrate than the hydration number, the crystal structure seems to be essentially the same as that of the tetrabutylammonium benzoate hydrate, which is tetragonal and has an ideal composition of $(n\text{-}C_4H_9)_4NOOCC_6H_5 \cdot 39.5H_2O$.[3]

The effect of the length and/or shape of an alkyl chain of a carboxylate anion on the stability of the group II hydrates are summarized as follows:

(1) Among the hydrates with R=C_4H_9, except for t-C_4H_9, the melting points of the pentanoate and the 3-methylbutanoate hydrate are approximately equal and higher than that of the 2-methylbutanoate hydrate (7.7 °C). This suggests that the methyl group attached to the carbon atom of 2-position causes a considerable distortion in the hydrogen-bonded water framework.

(2) The hydrates of the salt with $C_5H_{11}COO^-$ anion are generally unstable, as compared with those of the salt with $C_4H_9COO^-$ anion, presumably because the alkyl chain is a little too long to be accommodated stably within a water framework structure and, in addition, because of a distortion effect caused by the substituted methyl group. However, the 2-ethylbutanoate hydrate is exceptionally stable (mp=10.6 °C). This would partly be due to the fact that the main alkyl chain is shorter by either one or two carbon atoms than in the rest of the salts. Another interesting reason is that the distortion effect caused by a ethyl group attached to the carbon atom of 2-position is expected to be smaller than that caused by a methyl group, since the carbon atom of 2-position is connected with the small and flexible methylene group and not with the bulky methyl group.

(3) As is seen from Table 1, the pentanoate hydrate (mp=10.6 °C) is more stable than the 4-methylpentanoate hydrate (mp=6.0 °C). This indicates that the n-$C_4H_9COO^-$ ion can be more suitably enclathrated by the hydrogen-bonded water framework than the i-$C_5H_{11}COO^-$ ion, in striking contrast to the fact that, in the hydrates of ordinary tetraalkylammonium salts with the same inorganic anion like F^- tetraisopentylammonium salt hydrate is more stable than tetrabutylammonium salt hydrate.[7]

The formation of a clathrate-like hydrate for the tetrabutylammonium carboxylates with such long alkyl chains as n-$C_6H_{13}COO$-n-$C_{10}H_{21}COO^-$ is clearly confirmed from the phase diagrams shown in Fig. 3. The existence of these hydrates has never been known before. They are classified as the group III hydrates. The characteristic features of the group III hydrates are summarized as follows: (1) the hydration number is around 30; (2) the melting points are low; and (3) there is no simple relationship between the melting point and the alkyl chain length of the carboxylate anion. From the fact that the hydration number is around 30, the possible crystal structure of these hydrates would be isomorphous with a distorted $(n\text{-}C_4H_9)_4NF$ hydrate just as the group I hydrate. The main difference between the structure of the group I hydrate and that of the group III hydrate would be the existence of the interpenetration of a long alkyl chain into two or three pentagonal dodecahedra, which are face-sharing with each other, in the group III hydrate crystal.

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