Hydrates of Organic Compounds. XV. The Formation of Clathrate-Like Hydrates of Tetraisopentylammonium Alkanoates and Alkanedioates

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The solid-liquid phase diagrams of binary mixtures of water with tetraisopentylammonium alkanoates, $[(i\text{-}C_5H_{11})_4N]C_nH_{2n+1}COO$ (n=0—9), and with bis(tetraisopentylammonium) alkanedioates, $[(i\text{-}C_5H_{11})_4N]_2[OOC(CH_2)_nCOO]$ (n=0—10), were examined in order to confirm the formation of clathrate-like hydrates. The results are summarized as follows: (1) For all the compounds examined the formation of a clathrate-like hydrate is newly confirmed; (2) the melting points of these hydrates are fairly high (lie between 10 and 28 °C); (3) typical hydrates formed by the alkanoates have hydration numbers around 38 and those formed by the alkanedioates around 80; and (4) hydrates with hydration numbers around 14 and larger than 40 are also found for the alkanoate hydrates and around 30 and larger than 80 for the alkanedioate hydrates. The effects of the alkyl chain length of the alkanoate anion and of the methylene chain length of the alkanedioate anion on the stability of the hydrates are not marked, suggesting that a hydrogen-bonded framework of water molecules around a $(i\text{-}C_5H_{11})_4N^+$ cation is fairly stable.

Since the formation of unusual hydrates of tetrabutylammonium alkanoates and aromatic carboxylate like formate, acetate, propionate, and benzoate, which have a large number of water molecules per one ammonium ion (hydration numbers), was reported by Kraus et al.[1] in 1940, the formation of similar kind of alkanoate hydrates has extensively been studied.[2–5]

A single-crystal X-ray examination by Jeffrey and his co-workers on these hydrates[2–3] showed that they were clathrate-like hydrates similar to the so-called gas hydrates:[6] The water structure is a hydrogen-bonded framework and is essentially a regular arrangement of polyhedra-like pentagonal dodecahedra; tetrakaidecahedra and oxygen atoms of the carboxylate anion are incorporated into the water lattice, making an anionic host structure.

Recently, in our phase-diagrammatic studies[7–12] it was concluded that tetrabutylammonium alkanoates or alkanedioates having various alkyl chains or methylene chains could also form a clathrate-like hydrate. Judging from the hydration numbers and melting points of these hydrates, it was assumed that their crystal structure is isostructural with that of a well known $(n\text{-}C_4H_9)_4NF \cdot 30H_2O$ hydrate[13] and that the alkyl group of the alkanoate anions and a methylene chain of the alkanedioate anions is accommodated in a vacant pentagonal dodecahedra.

On the other hand, although some tetraisopentylammonium salts, such as $(i\text{-}C_5H_{11})_4NF$ and $(i\text{-}C_5H_{11})_4NCl$, are known to form similar type hydrates,[2,14,15] no information concerning the formation of a clathrate-like hydrate of tetraisopentylammonium alkanoates or alkanedioates has been reported, except for formate[1] and benzoate.[4] Thus, in this work, phase-diagrammatic studies regarding binary mixtures of tetraisopentylammonium alkanoates or alkanedioates with water were carried out in order to confirm the formation of clathrate-like hydrates. Tetraisopentylammonium alkanoates and alkanedioates are expected to form more stable hydrates than those of tetrabutylammonium alkanoates or alkanedioates since (1) the water frameworks surrounding a $(i\text{-}C_5H_{11})_4N^+$ cation are, in general, more stable than those surrounding a $(n\text{-}C_4H_9)_4N^+$ cation[16] and (2) in a $(i\text{-}C_5H_{11})_4NF$ hydrate,[14] there exists an extended layer structure of connected pentagonal dodecahedra which are suitable to accommodate either an alkyl chain of an alkanoate anion or a methylene chain of an alkanedioate anion.

Experimental

Aqueous solutions of tetraisopentylammonium alkanoates, except for formate and acetate, were prepared by a reaction between tetraisopentylammonium iodide and the corresponding silver alkanoates in water, followed by filtration of silver iodide precipitate. Tetraisopentylammonium iodide was synthesized by allowing a reaction of triisopentylamine with isopentyl iodide in ethyl acetate and purified by repeated recrystallization from ethyl acetate. Each silver alkanoate was obtained as a precipitate by mixing an aqueous solution of silver nitrate with an aqueous solution of sodium alkanoate, followed by repeated washing with water in order to remove the resultant sodium nitrate. Aqueous solutions of tetraisopentylammonium formate, acetate and of all the bis(tetraisopentylammonium) alkanedioates, were obtained by neutralization of tetraisopentylammonium hydroxide solution with the corresponding acids. The hydroxide solution was obtained by treating tetraisopentylammonium iodide with freshly prepared silver(I) oxide in water. The wet silver(I) oxide was prepared by reacting a silver nitrate solution with a sodium hydroxide solution, followed by filtration and repeated washing with water. Triisopentylamine, isopentyl iodide and all the carboxylic acids and some of the dicarboxylic acids were reagent grade commercial materials and used without further purification. Seven dicarboxylic acids, $HOOC(CH_2)_nCOOH$ with n=3—8 and 10, which were purchased from Tokyo Kasei Kogyo Co., Ltd., were recrystallized from water.

The solid-liquid phase diagrams of the binary tetraisopentylammonium alkanoate (or alkanedioate)-water systems were determined in the following manner. A sample solution (about 1.0—1.5 g) of known concentration was prepared by weighing out water and a concentrated mother solution of each alkanoate (or alkanedioate), and was sealed in a small glass ampoule. The concentration of the mother solution was determined by a titration method using a sodium tetraphenylborate solution.[9] Each ampoule was gradually cooled until the solid phase appeared and was annealed for at least 24 h at a temperature several degrees lower than the temperature at which the solid phase completely disssolved. After that, the ampoule was slowly warmed (at the rate of about 0.3—0.5 °C per hour) with shaking in a constant temperature bath and the temperature at which the solid phase completely dissolved was accurately determined.

Results and Discussion

(1) The Formation of Hydrates of Tetraisopentylammonium Alkanoates. The solid-liquid phase diagrams for the binary systems, water-$[(i\text{-}C_5H_{11})_4N]n\text{-}C_nH_{2n+1}COO$, where n=2—5, are shown in Fig. 1. The logarithm of the concentration expressed as the 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 the figure. The phase diagrams of two binary systems, water-$[(i\text{-}C_5H_{11})_4N]HCOO$ and water-$[(i\text{-}C_5H_{11})_4N]CH_3COO$, are not shown in Fig. 1 since the phase diagram of the former system resembles the one of the water-$[(i\text{-}C_5H_{11})_4N]C_2H_5COO$ system and the latter system the one of the water-$[(i\text{-}C_5H_{11})_4N]n\text{-}C_3H_7COO$ system. The phase diagrams of these systems exhibit congruent melting points at concentrations near X=0.025—0.026, indicating that these carboxylates form a hydrate with hydration numbers around 38. It is interesting to note that (1) these hydrates are fairly stable: the melting points are 22—28 °C; and (2) they can be in equilibrium with very dilute solutions: For

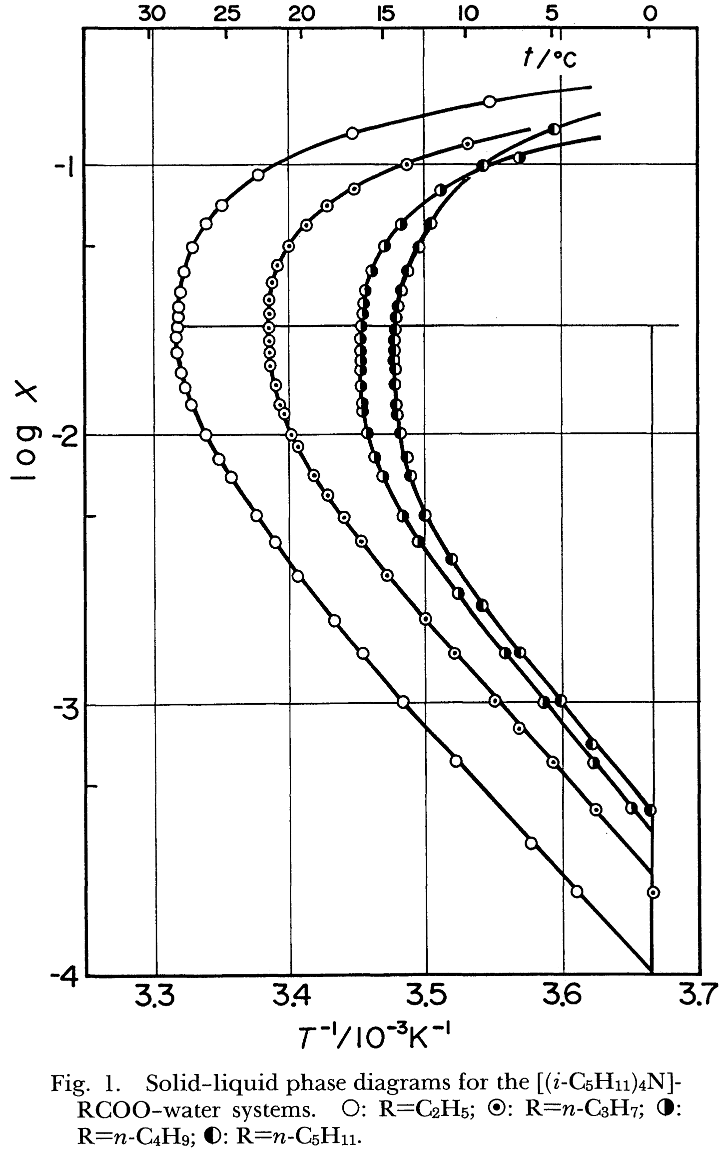

Fig. 1. Solid-liquid phase diagrams for the $[(i\text{-}C_5H_{11})_4N]$-RCOO-water systems. ○: R=C_2H_5; ⊙: R=$n\text{-}C_3H_7$; ◑: R=$n\text{-}C_4H_9$; ◐: R=$n\text{-}C_5H_{11}$.

example, the most stable $[(i\text{-}C_5H_{11})_4N]C_2H_5COO$ hydrate is formed in such a dilute solution as $X=1\times10^{-4}$ (0.206 wt%).

The phase diagrams of the two systems with $n=4$ and $n=5$ also exhibit congruent melting points at about 15 °C. However, all the solid phases which are formed in the solutions in the concentration range between $X=0.020$ and $X=0.024$ for $n=4$ salt and between $X=0.018$ and 0.024 for $n=5$ salt dissolve at very narrow temperature range: Between a maximum dissolution temperature and the one only 0.1 °C lower than that. Therefore, exact hydration numbers cannot be determined for these hydrates. A probable reason for this behavior is that some hydrates with different hydration numbers between 40 and 55 are formed simultaneously, depending upon the concentration of the solution. The fact that the slope $-\partial \log X/\partial(1/T)$ in dilute solutions, $X=0.001$ for example, for the above-mentioned two systems, is slightly steeper than that of the systems of $n=2$ and $n=3$ indicates that salts with $n=4$ and $n=5$ form a hydrate with hydration numbers larger than those of $n=2$ and 3 hydrates (around 38), since it has been verified that the slope $-\partial \log X/\partial(1/T)$ is approximately proportional to the hydration numbers of a hydrate.[16]

The solid-liquid phase diagrams for binary systems water-$[(i\text{-}C_5H_{11})_4N]n\text{-}C_nH_{2n+1}COO$ with long alkyl chains as $n=6$ and 9 are shown in Fig. 2. For a comparison, Fig. 2 includes the phase diagram of the $n=2$ system shown in Fig. 1. The phase diagram of a system with $n=7$ is omitted because of the similarity in the data with those of the $n=6$ system. This figure shows the existence of congruent melting points near $X=0.026$, just as in the case of $n=2$, indicating that salts with such long alkyl chains as $n=6$, 7, and 9 can also form a hydrate with hydration numbers around 38, although their melting points (11—16 °C) are

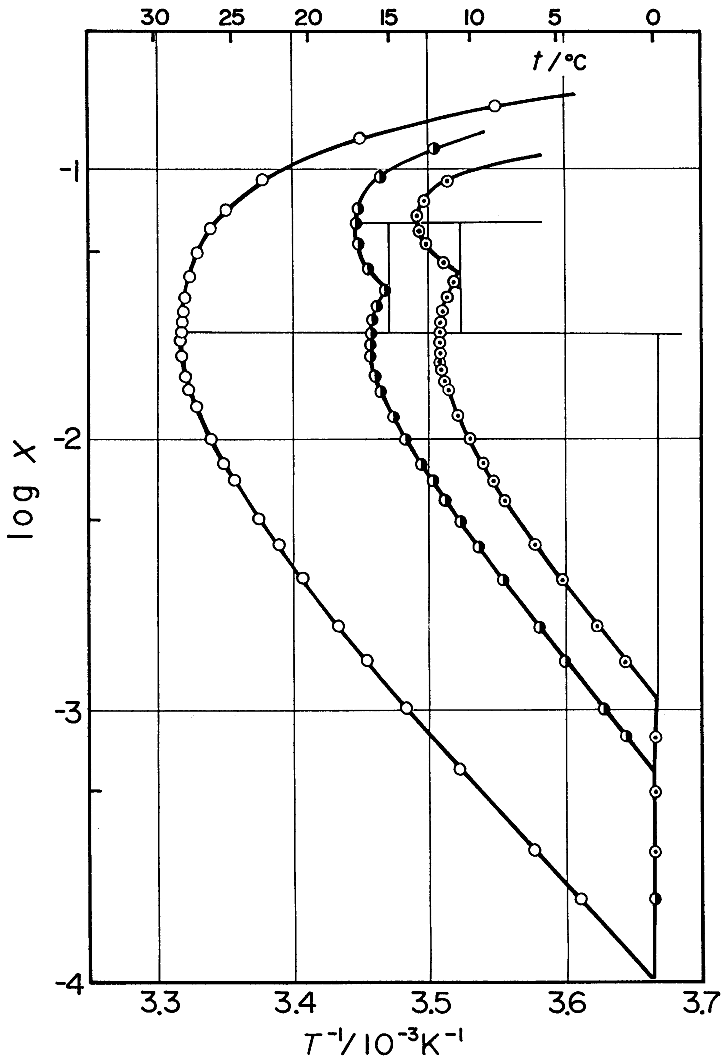

Fig. 2. Solid-liquid phase diagrams for the $[(i\text{-}C_5H_{11})_4N]$-RCOO-water systems. ○: $R=C_2H_5$; ⊙: $R=n\text{-}C_6H_{13}$; ◑: $R=n\text{-}C_9H_{19}$.

lower than those of the salts with short alkyl chains like n=0—3 (Fig. 1). Furthermore, Fig. 2 indicates that systems with n=6, 9 (and n=7) have another congruent melting point around X=0.067. This means the formation of hydrate with hydration numbers around 14. It is interesting to note that these hydrates have slightly higher melting points than those with hydration numbers around 38.

All of the melting points and hydration numbers, determined from each congruent melting point and congruent composition, are summarized in Table 1.

Table 1. Melting Points and Hydration Numbers of the Clathrate-Like Hydrates Formed by a Series of Tetraisopentylammonium Alkanoates, $[(i\text{-}C_5H_{11})_4N]RCOO$

R	Melting point t_m/ °C	Hydration numbers
H	22.4	37±3
CH_3	24.5	37±2
C_2H_5	28.3	39±2
$n\text{-}C_3H_7$	22.3	39±2
$n\text{-}C_4H_9$	16.5	40—50
$n\text{-}C_5H_{11}$	14.3	40—55
$n\text{-}C_6H_{13}$	11.9	40±2
	13.4	14±1
$n\text{-}C_7H_{15}$	10.7	37±2
	13.1	14±2
$n\text{-}C_9H_{19}$	16.1	37±3
	17.1	15±2

The existence of these hydrates, except for the formate hydrate, has been newly confirmed in this study. However, the melting point 15—20 °C and hydration numbers 50 of the formate hydrate reported by Kraus et al.[1] are fairly different from our values. From Table 1 it is clear that the most typical hydrate is one with hydration numbers around 38. This hydrate is formed regardless of the chain length of the alkyl group in the alkanoate anion and the effect of the chain length of the $C_nH_{2n+1}COO^-$ anion on the melting points of the hydrates is not so marked. Judging from the values of the hydration numbers and the melting points, these hydrates seem to be isostructural clathrate-like hydrates with a well known $(i\text{-}C_5H_{11})_4NF \cdot 39H_2O$ hydrate.[14] Other hydrates found in Table 1 are the ones with hydration numbers larger than 40 and around 14. The former is formed for the salts of n=4 and 5 and the latter for the salts with a longer alkanoate than n=6. Although there is no information concerning the structure of these hydrates, it seems probable that one of the former hydrates has some connection with a tetraisopentylammonium benzoate hydrate, $[(i\text{-}C_5H_{11})_4N]C_6H_5COO \cdot (48\pm2)H_2O$, which was found in a preliminary experiment. This hydrate is fairly unstable with a melting point of about 6.3 °C.

In Fig. 3 the relationship between the melting points of the hydrates and the number of carbon atoms of the alkyl group in the carboxylate anion (n) is shown for the two series of salts, $[(i\text{-}C_5H_{11})_4N]\text{-}n\text{-}C_nH_{2n+1}COO$ and $[(n\text{-}C_4H_9)_4N]n\text{-}C_nH_{2n+1}COO$.[7]

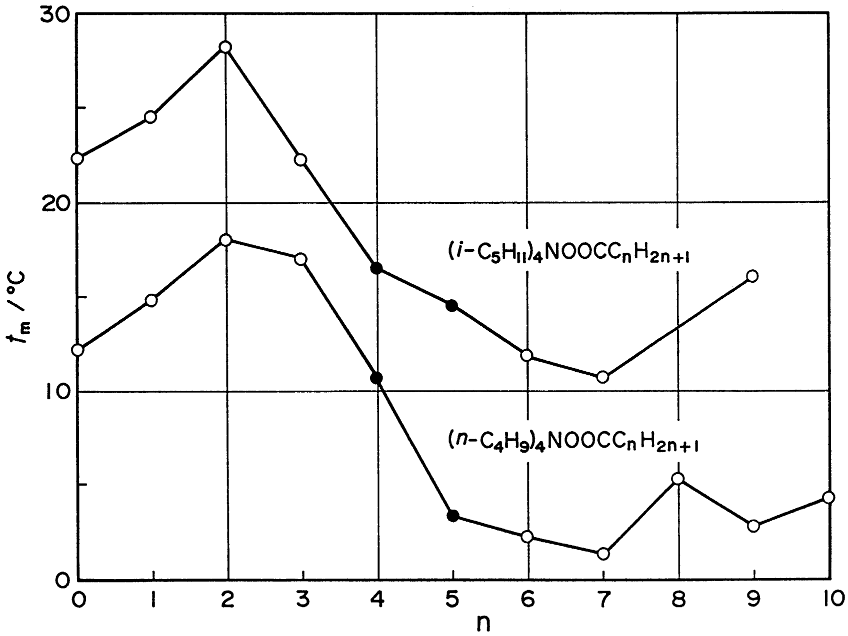

Fig. 3. Relationships between the melting points, t_m, of the tetrabutylammonium and of the tetraisopentylammonium alkanoate hydrates and the chain length of the alkanoate anion. Filled circle indicates a hydrate with somewhat larger hydration numbers as compared with the other hydrates shown by open circles.

The latter series form hydrates with hydration numbers around 30 and only when n=4 and 5, just as in the case of the former salt hydrates, hydrates with hydration numbers larger than 30 are formed.[7] It is interesting to note that both series of hydrates behave almost in a similar manner, except that the melting points of a series of $[(i\text{-}C_5H_{11})_4N]n\text{-}C_nH_{2n+1}COO$ hydrates are about 10 °C higher than those of a series of $[(n\text{-}C_4H_9)_4N]n\text{-}C_nH_{2n+1}COO$ hydrates irrespective of the values of n, coinciding with a general trend that the water frameworks surrounding a $(i\text{-}C_5H_{11})_4N^+$ cation are more stable than those surrounding a $(n\text{-}C_4H_9)_4N^+$ cation.[12,16] The similar behavior of the two series of hydrates leads the conclusion that the same arguement can be applied regarding the way to accommodate an alkyl group, $n\text{-}C_nH_{2n+1}$, of the alkanoate anion within the $[(i\text{-}C_5H_{11})_4N]n\text{-}C_nH_{2n+1}COO$ hydrates as in the $[(n\text{-}C_4H_9)_4N]n\text{-}C_nH_{2n+1}COO$ hydrates:[7-10] (1) Such short alkyl groups as CH_3, C_2H_5, and $n\text{-}C_3H_7$ are encaged in a vacant pentagonal dodecahedron, which exists in a gap between the arrangement of larger polyhedra (tetrakaidecahedra and/or pentakaidecahedra) filled by one of the isopentyl group of a tetraisopentylammonium cation and the highest melting point of the propionate hydrate coincide with the best fitness of the $CH_3CH_2COO^-$ anion to a pentagonal dodecahedron; (2) long alkyl chains like $n\text{-}C_4H_9$—$n\text{-}C_9H_{19}$ penetrate through two (or three) vacant pentagonal dodecahedra forming a hydrogen-bonded anionic host structure with water.

(2) The Formation of Hydrates of Bis(tetraisopentylammonium) Alkanedioates. The solid-liquid phase diagrams for the binary systems, water-$[(i\text{-}C_5H_{11})_4N]_2OOC(CH_2)_nCOO$, where n=0—2 are shown in Fig. 4 in the same manner as in Figs. 1 and 2. All three systems exhibit congruent melting points (20—25 °C) at concentrations around X=0.0125, indicating

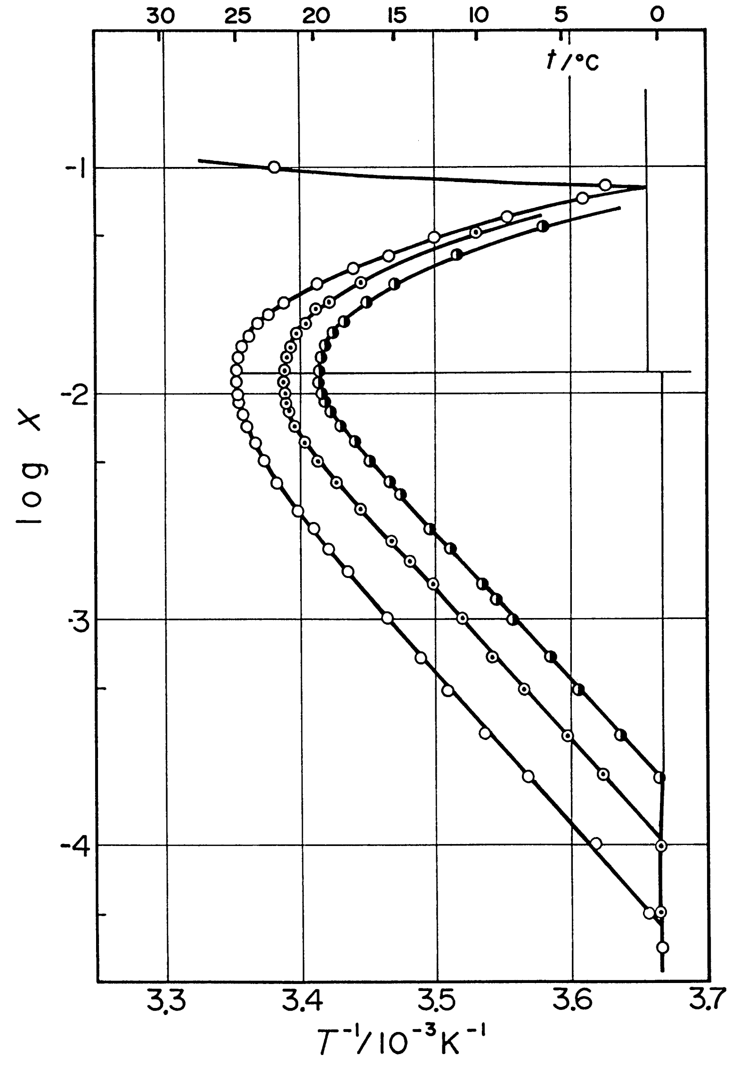

Fig. 4. Solid-liquid phase diagrams for the water-$[(i\text{-}C_5H_{11})_4N]_2OCC(CH_2)_nCOO$ systems. ○: n=0; ⊙: n=1; ◑: n=2.

that these salts form a fairly stable hydrate with hydration numbers of about 80. The melting points of the hydrates decrease with increasing the number of n. The solid-liquid phase diagrams for the other three systems with n=3—5 show similar behaviors as shown in Fig. 4, except that the most stable hydrate is formed by the salt of n=4; its melting point is 27.5 °C.

On the other hand, the solid-liquid phase diagrams, which are shown in Fig. 5, for the binary systems, water-$[(i\text{-}C_5H_{11})_4N]_2OOC(CH_2)_nCOO$, where n=6—10, exhibit a somewhat complicated behavior, as compared with the case of n=0—5. The characteristic features of Fig. 5 are summarized as follows: (1) Although there is a maximum dissolution temperature around X=0.0125 for the salts of n=6—8, solid phases formed from the solutions in the concentration range of X=0.012—0.013 for the n=6 salt, X=0.012—0.014 for n=7, and X=0.010—0.0125 for n=8, dissolve at very narrow temperature range around the maximum dissolution temperatures just as in the case of the alkanoate hydrates with n=4 and n=5 (Fig. 2). This indicates that exact hydration numbers of the hydrates cannot be determined. (2) There are incongruent melting points about 1 °C below the maximum dissolution temperature. These temperatures are 18.3 °C for the n=6 salt, 17.2 °C for the n=7 salt and two or three incongruent melting points between 17 and 19 °C for the n=10 salt. The existence of incongruent compositions smaller than X=0.012 clearly indicates the formation of hydrates with hydration numbers larger than 80. (3) For the systems of n=8 and n=10, another congruent melting point is found around X=0.032; this means the formation of a hydrate with hydration numbers around 30.

The melting points and hydration numbers found for the hydrates of a series of bis(tetraisopentylammonium) alkanedioate are summarized in Table 2. All of these hydrates were newly confirmed in this study.

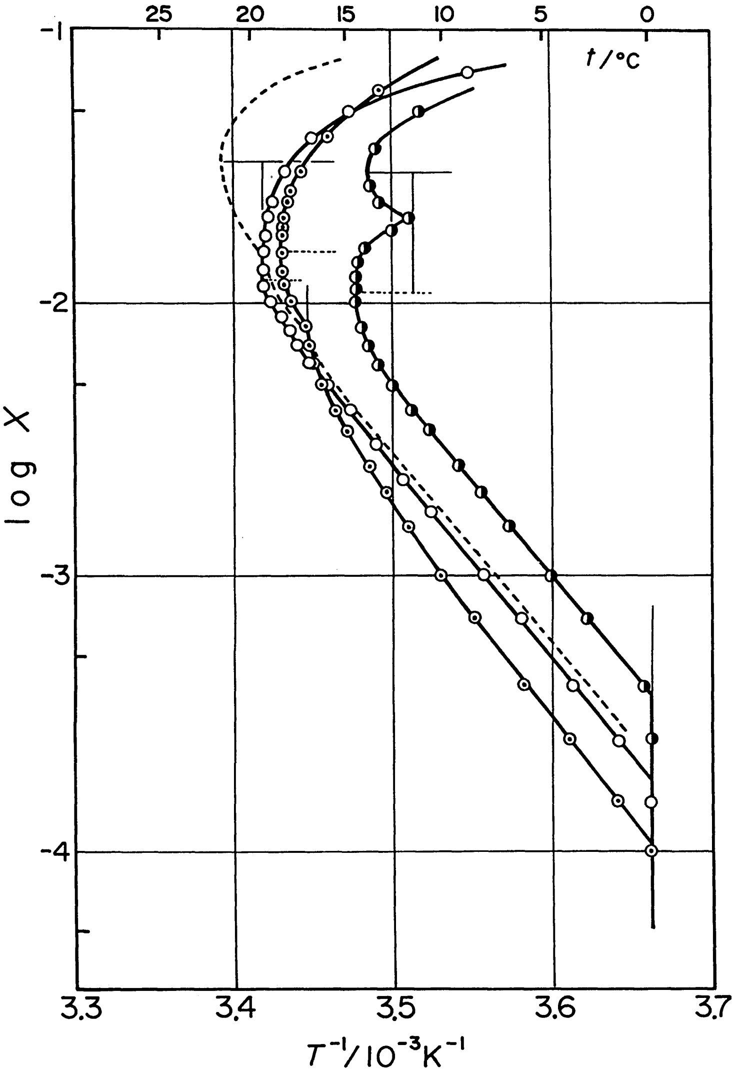

Fig. 5 Solid-liquid phase diagrams for the water-$[(i\text{-}C_5H_{11})_4N]_2$ $OOC(CH_2)_nCOO$ systems. ○: n=6; ⊙: n=7; ◑: n=8; broken line: n=10.

As can be seen in Table 2, the most typical hydrate is one with a hydration number around 80. This hydrate is considered to be isostructural with the alkanoate hydrates of hydration numbers around 38 (Table 1), since the hydration number, 80, is about twice of 38. Other hydrates are those with hydration numbers around 30 and larger than 80. As mentioned above, the exact hydration numbers of the latter hydrates cannot be determined owing to the complexity of the phase diagrams. It is not certain whether there is any structural relation between these hydrates and the alkanoate hydrates having hydration numbers larger than 40 (Table 1). The hydrate of the hydration numbers around 30 is formed for alkanedioates with n larger than 8 and, eventually, its hydration numbers are almost twice that (14—15, Table 1) of the alkanoate hydrates which are formed by the alkanoates with n larger than 6. Both hydrates seem to be isostructural with each other.

Table 2. Melting Points and Hydration Numbers of the Clathrate-Like Hydrates Formed by a Series of Bis(tetraisopentylammonium) Alkanedioates, $[(i\text{-}C_5H_{11})_4N]_2OOC(CH_2)_nCOO$

n	Melting point t_m/°C	Hydration numbers
0	25.1	80±2
1	22.1	80±2
2	19.8	82±2
3	23.7	79±3
4	27.5	80±3
5	19.8	80±3
6	19.4	75—85
	18.3 (incong.)	
7	18.4	70—85
	17.2 (incong.)	
8	14.5	80—100
	13.9	32±3
10	21.5	30±5

The relationship between the melting points, t_m, of the alkanedioate hydrates and the methylene chain length, n, of the alkanedioate anions is shown in Fig. 6 for two series of alkanedioates, $[(i\text{-}C_5H_{11})_4N]_2OOC(CH_2)_nCOO$ and $[(n\text{-}C_4H_9)_4N]_2OOC(CH_2)_nCOO$.[11] In general, the t_m's vary with n in a similar manner for both series of hydrates. Just as in the case of alkanoate hydrates (Fig. 3), the melting points of the tetraisopentylammonium dicarboxylate hydrates are about 10 °C higher than those of the tetrabutylammonium alkanedioate hydrates, though this difference becomes larger when n is larger than 6. The maximum t_m is found in the case n=4 for the bis(tetraisopentylammonium) alkanedioate hydrates whereas n=3 for the bis(tetrabutylammonium) alkanedioate hydrates. This discrepancy will not be essential since the melting point of the hydrate of bis(tetrabutylammonium) alkanedioate with n=4 is also fairly high.

It is interesting to note that the melting points initially decrease with increasing n from 0 to 2 then increase with increasing n from 2 to 4. This can be explained by the fact that the hydrates of salts with such small n as 0—2 are constructed with two kinds of units, $[[(i\text{-}C_5H_{11})_4N]OOC(CH_2)_nCOO]^-$ and (i-

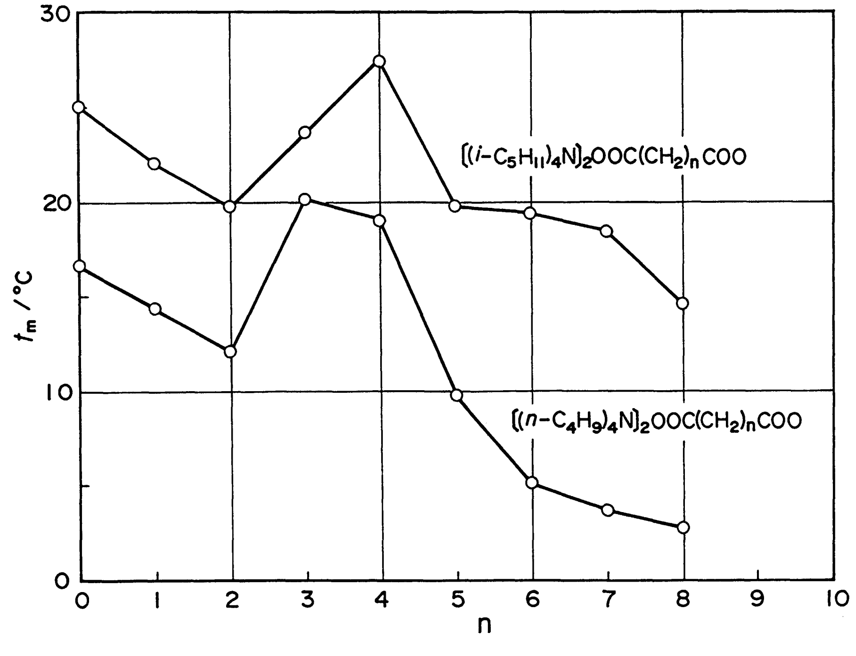

Fig. 6. Relationships between the melting points, t_m, of the bis(tetrabutylammonium) and of the bis(tetraisopentylammonium) alkanedioate hydrates and of the chain length of the methylene chain in the alkanedioate anion.

$C_5H_{11})_4N^+$; then, the distortion effect of the $^-OOC(CH_2)_nCOO^-$ anion on the hydrogen-bonded water network surrounding a $(i\text{-}C_5H_{11})_4N^+$ cation increases with increasing n, leading to a lowering of the melting points of the hydrates. On the other hand, the hydrates of the salts with n larger than 3 can be considered to be constructed by a sequence of $(i\text{-}C_5H_{11})_4N^+ \cdots {}^-OOC(CH_2)_nCOO^- \cdots (i\text{-}C_5H_{11})_4N^+$; the central $^-OOC(CH_2)_nCOO^-$ anion is surrounded by vacant pentagonal dodecahedron or connected pentagonal dodecahedra, leading to the formation of fairly stable hydrate, as is found in the case of tetraisopentylammonium alkanoate hydrates.

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