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Hydrates of Organic Compounds. XVI.
Determination of the Melting Points and Hydration Numbers of the Hydrates of Tetrabutyl(or Tetraisopentyl)ammonium Alkanesulfonates

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The solid-liquid phase diagrams of binary mixtures of water with tetraisopentylammonium alkanesulfonates, $[(i\text{-}C_5H_{11})_4N][n\text{-}C_nH_{2n+1}SO_3]$ (n=1—8), bis(tetrabutylammonium) alkanedisulfonates, $[(n\text{-}C_4H_9)_4N]_2[O_3S(CH_2)_nSO_3]$ (n=2—5), and with bis(tetraisopentylammonium) alkanedisulfonates, $[(i\text{-}C_5H_{11})_4N]_2[O_3S(CH_2)_nSO_3]$ (n=2—5), were examined in order to confirm the formation of hydrates. For all of the sulfonates examined the formation of hydrates has been newly confirmed. The hydrates of the tetraisopentylammonium alkanesulfonates have hydration numbers of around 37—40 and fairly high melting points (lie between 13 and 19 °C). The typical hydrates formed by the bis(tetrabutylammonium) alkanedisulfonates have hydration numbers of around 52 and those by the bis(tetraisopentylammonium) alkanedisulfonates around 76. The former disulfonate hydrates have low melting points (between 1.0 and 10 °C). However, the latter disulfonate hydrates have fairly high melting points (between 13 and 18 °C). A salt with n=4 forms the most stable hydrate for both series of alkanedisulfonates. Judging from the hydration numbers and melting points, these hydrates seem to be clathrate-like.

It is well-known that some tetrabutylammonium and tetraisopentylammonium salts, such as $(n\text{-}C_4H_9)_4NF$ and $(i\text{-}C_5H_{11})_4NF$, can form unusual hydrates which have a large number of water molecules per one ammonium ion (hydration numbers) as well as fairly high melting points between 0 °C and room temperature.[1—3] According to a single-crystal X-ray examination by Jeffrey and co-workers[2—5] these hydrates were semi-clathrate hydrates, similar to the so-called gas hydrates:[4] The water structure is a hydrogen-bonded framework, and is essentially a regular arrangement of polyhedra, such as pentagonal dodecahedra and tetrakaidecahedra; each alkyl group of an ammonium cation is incorporated into one of the polyhedra.[2—3]

The formation of similar types of hydrates has also been known for various tetrabutylammonium (or tetraisopentylammonium) salts which have organic anions like alkanoates[5—11] and dialkanoates.[11,12] These hydrates are of special interest, since their atability and structure are affected not only by the type of tetraalkylammonium cation, but also by the hydrocarbon portion of the anion. Recently, from the fact that tetrabutylammonium alkanedioates, $[(n\text{-}C_4H_9)_4N]_2[OOC(CH_2)_nCOO]$, can form a stable clathrate-like hydrate when n=3,[12] the possibility to form a hydrate of tetrabutylammonium polyacrylate was both anticipated and verified.[13] The formation of a hydrate of such a polymeric salt has never been known before.

Another polyanion which is expected to possibly form a similar type hydrate is a polysulfonate anion, such as the poly(ethenesulfonate) anion and the poly(styrenesulfonate) anion. However, there is no basic information about the formation of hydrates of tetraalkylammonium alkanesulfonates and alkanedisulfonates, except for a series of tetrabutylammonium alkanesulfonates.[14] Thus, in this work, phase-diagrammatic studies regarding binary mixtures of water with tetraisopentylammonium alkanesulfonates, bis(tetrabutylammonium)alkanedisulfonates, or bis(tetraisopentylammonium) alkanedisulfonates were carried out in order to confirm the formation of clathrate-like hydrates and, when formed, to determine the effect of the hydrocarbon portion of the anion on the melting points and hydration numbers.

Experimental

Aqueous solutions of tetraisopentylammonium alkanesulfonates, $[(i\text{-}C_5H_{11})_4N][n\text{-}C_nH_{2n+1}SO_3]$ (n=1—6, and 8), bis(tetrabutylammonium) alkanedisulfonates, $[(n\text{-}C_4H_9)_4N]_2[O_3S(CH_2)_nSO_3]$ (n=2—5), and of bis(tetraisopentylammonium) alkanedisulfonates, $[(i\text{-}C_5H_{11})_4N]_2[O_3S(CH_2)_nSO_3]$ (n=2—5), were prepared by neutralization of either an aqueous tetrabutylammonium hydroxide solution or an aqueous tetraisopentylammonium hydroxide solution with the corresponding sulfonic acid solutions. The hydroxide solutions were obtained by treating either tetrabutylammonium iodide or tetraisopentylammonium iodide with freshly prepared silver(I) oxide in water followed by filtration of the AgI precipitate. Tetrabutylammonium iodide was prepared by precipitation from an aqueous solution of tetrabutylammonium bromide (purchased from Tokyo Kasei Kogyo Co., Ltd.) with the addition of sodium iodide, followed by washing with water and air-drying in a desiccator. The iodide was purified by repeated recrystallization from ethyl acetate. Tetraisopentylammonium iodide was synthesized and purified in the same manner as described in a previous paper.[11] All of the sulfonic acid solutions, except for CH_3SO_3H and $C_2H_5SO_3H$, were obtained by passing each sodium salt solution through a column of cation-exchange resin (Amberlite IR-120B) converted, in advance, into the acid form by about a 2 mol dm^{-3} hydrochloric acid solution. Two acids, CH_3SO_3H and $C_2H_5SO_3H$, and the sodium salts $n\text{-}C_nH_{2n+1}SO_3Na$ with n=5, 6, and 8, were purchased either from Tokyo Kasei Kogyo Co., Ltd. or Aldrich Chemical Co., Inc.. Two sodium salts, $n\text{-}C_nH_{2n+1}SO_3Na$ with n=3 and 4, were synthesized in the manner reported by Reed et al.[15] A half mole of the corresponding alkyl iodide was slowly added to a hot saturated aqueous solution of one mole of sodium sulfite. The mixture was refluxed for a few days. After the water had been evaporated under reduced pressure, the reaction product was extracted with hot ethanol. The sodium salt was purified by repeated recrystallization from ethanol. Two sodium alkanedisulfonates, $NaO_3S(CH_2)_nSO_3Na$ with n=2 and 4, were purchased from Tokyo Kasei Kogyo Co., Ltd., and two other sodium salts with n=3 and 5 were synthesized using the corresponding dibromide, $Br(CH_2)_nBr$ (n=3 or 5), by a similar manner as discribed above.[16] All of the synthesized disodium salts were confirmed by their NMR and IR spectra.

The solid–liquid phase diagrams for the binary systems of water–each sulfonate mentioned above were determined in the same manner as described in previous papers.[8–11] The concentration of each mother solution was determined by measuring the amount of either tetrabutylammonium cation or tetraisopentylammonium cation by titration with a sodium tetraphenylborate solution standardized by pure $(n\text{-}C_4H_9)_4NI$ solid.

Results and Discussion

(1) The Formation of Hydrates of Tetraisopentylammonium Alkanesulfonates. The solid–liquid phase diagrams for the binary systems, water–$[(i\text{-}C_5H_{11})_4N][n\text{-}C_nH_{2n+1}SO_3]$, where n=1—3, 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 phase diagrams of the salts with n=1 and 2 exhibit congruent melting points at concentrations near X=0.025, indicating that these two salts form a hydrate with hydration numbers around 39. These hydrates are fairly stable: The melting points are 18.7 °C (n=1) and 17.6 °C (n=2), respectively. It is interesting to note that the formation of these hydrates occurs in very dilute solutions (around $X=5\times10^{-4}$), just as found for other tetraisopentylammonium salt hydrates.[11,17]

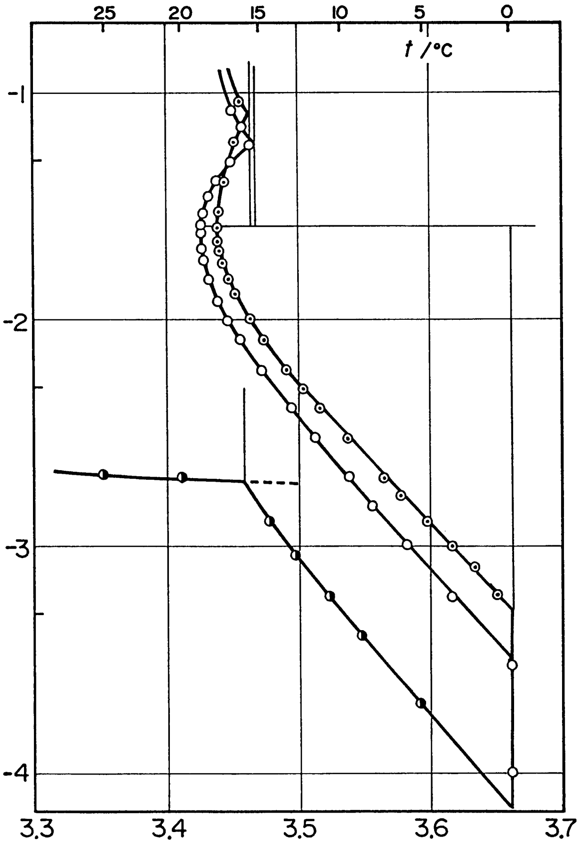

Fig. 1. Solid–liquid phase diagrams for the water–$[(i\text{-}C_5H_{11})_4N][n\text{-}C_nH_{2n+1}SO_3]$ systems. ○: n=1; ⊙: n=2; ◑: n=3.

In the n=3 system, two kinds of solid–liquid equilibrium lines intersect each other at around X=0.002 and 16.1 °C. The line at temperatures below 16.1 °C may be regarded as being an equilibrium line between a hydrate solid and an aqueous solution, just as in the case of the other two salts with n=1 and 2, since the slopes $-\partial \log X/\partial(1/T)$ are almost the same for these three systems: It has been verified that this slope is approximately proportional to the hydration numbers of the hydrate.[18] Thus, it can be concluded that the salt with n=3 forms a hydrate with hydration numbers around 39 at temperatures below 16.1 °C. Its melting point is estimated to be 22—23 °C if the hydrate were stable above 16.1 °C. The line at temperatures above 16.1 °C seems to exhibit an equilibrium between an anhydrous $[(i\text{-}C_5H_{11})_4N][n\text{-}C_3H_7SO_3]$ solid and a saturated solution. It is interesting to note that although the salt with n=3 can form a fairly stable hydrate, its anhydrous salt is more stable at temperatures above 16.1 °C.

The phase diagrams for the salts with n=4 and 5 are essentially the same as those of n=1 and 2 shown in Fig. 1, except that for the salt with n=5; in this case a region in which two liquid phases are in equilibrium appears above 20.9 °C. The critical concentration is almost the same as the congruent composition of its hydrate (X=0.025).

The phase diagrams for the salts with n=6 and 8 are shown in Fig. 2. For these two systems, the liquid–liquid equilibrium region extends towards the wide-concentration range and the low-temperature region. The solid–liquid phase diagram for the n=6 system intersects with its liquid–liquid phase diagram at X=0.067, which is greater than its congruent composition (X=0.024). However, for the n=8 system these two lines intersect at a concentration (X=0.01) before the solid–liquid line reaches its congruent composition. As a result of this, the melting point and hydration numbers for the hydrate of the n=8 salt cannot be determined exactly, though a similar hydrate to that of the n=6 salt is undoubtedly formed at concentrations below X=0.01 for the same reason as mentioned regarding the n=3 system. Its melting point is estimated to be 14—15 °C.

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

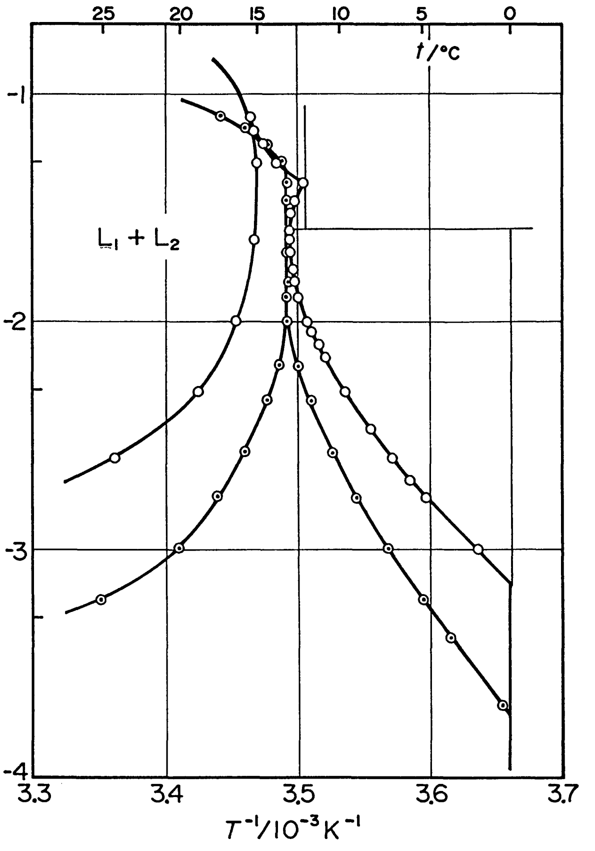

Fig. 2. Solid–liquid phase diagrams for the water–$[(i\text{-}C_5H_{11})_4N][n\text{-}C_nH_{2n+1}SO_3]$ systems. ○: n=6; ⊙: n=8.

Table 1. Melting Points and Hydration Numbers of the Clathrate-Like Hydrates Formed by a Series of Tetraisopentylammonium Alkanesulfonates, $[(i\text{-}C_5H_{11})_4N][n\text{-}C_nH_{2n+1}SO_3]$

n	Melting point t_m/°C	Hydration numbers
1	18.7	39±2
2	17.6	39±2
3	(22—23)[a]	—
4	18.3	37±2
5	17.8	40±2
6	13.1	37±2
8	(14—15)[a]	—

a) See text.

together with estimated melting points for the hydrates of the salts with n=3 and 8. The existence of these hydrates has been newly confirmed in this study. From Table 1 it is clear that all of the hydrates have hydration numbers around 39. As mentioned above, the hydrates formed by the salts with n=3 and 8 presumably have similar hydration numbers. It is interesting to note that the same type of hydrate is formed regardless of the chain length of the alkyl group in the alkanesulfonate anion. The melting points of these hydrates are fairly high (higher than 17 °C, except for the hydrates of n=6 and 8) and the effect of the chain length of the $C_nH_{2n+1}SO_3^-$ anion on the melting points of these hydrates is not so marked. Judging from the values of the hydration numbers and the melting points, these hydrates seem to be an isostructural clathrate-like hydrate with a well-known $(i\text{-}C_5H_{11})_4NF \cdot 39H_2O$ hydrate, whose structure has been examined in detail by Jeffrey and his co-worker.[3]

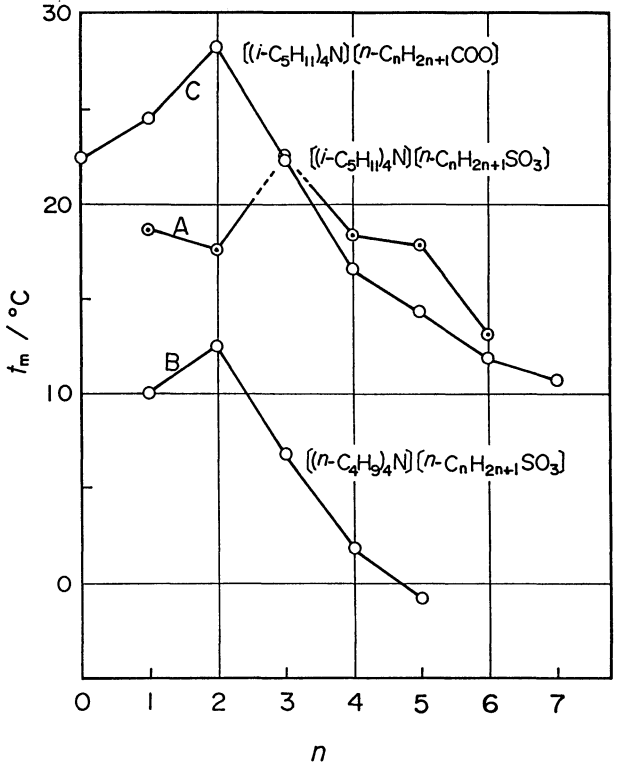

Fig. 3. Relationships between the melting points, t_m, of the hydrates of tetraisopentylammonium alkanesulfonates (A), tetrabutylammonium alkanesulfonates (B), and of tetraisopentylammonium alkanoates (C) and the number of carbon atoms, n, of either alkanesulfonate or alkanoate anion.

In Fig.3 the relationships between the melting points (t_m) of the hydrates and the number of carbon atoms of the alkyl group in the anion (n) is shown (A), together with those of two related salts of $[(n\text{-}C_4H_9)_4N][n\text{-}C_nH_{2n+1}SO_3]$ (B)[14] and $[(i\text{-}C_5H_{11})_4N][n\text{-}C_nH_{2n+1}COO]$ (C).[11] A comparison of line A with line B clearly indicates that the hydrates of tetraisopentylammonium alkanesulfonates are more stable than those of tetrabutylammonium alkanesulfonates: The melting points of the former hydrates are more than 15 degrees higher than those of the latter hydrates when n is larger than 3. This fact suggests that a hydrogen-bonded framework of water molecules surrounding an $(i\text{-}C_5H_{11})_4N^+$ cation is fairly stable, compared with that around an $(n\text{-}C_4H_9)_4N^+$ cation, as has been pointed out in other studies.[11,18] It is interesting to note that when n=1 and 2 the melting points of a series of tetraisopentylammonium alkanesulfonates (A) are 6—10 °C lower than those of a series of tetraisopentylammonium alkanoates (C). As discussed in an earlier paper,11) the highest melting point of the $[(i\text{-}C_5H_{11})_4N][C_2H_5COO]$ hydrate is explained by the best fit of the $C_2H_5COO^-$ anion to a pentagonal dodecahedron, which exists in a gap between the arrangement of larger polyhedra filled by one of the isopentyl groups of a tetraisopentylammonium cation. For the sulfonate hydrates with n=1 and 2, however, the distortion of the hydrogen-bonded water network which incorporates sulfonate anions, like $CH_3SO_3^-$ and $C_2H_5SO_3^-$, will be greater than when incorporates such alkanoate anions as CH_3COO^- and $C_2H_5COO^-$ because of the bulkiness of the SO_3^- group, compared with the COO^- group. This leads to a lowering of the melting points of the hydrates of $[(i\text{-}C_5H_{11})_4N][CH_3SO_3]$ and $[(i\text{-}C_5H_{11})_4N][C_2H_5SO_3]$.

Another feature which can be seen from a comparison of lines A and C in Fig.3 is the fact that when n is larger than 3 the melting points of both series of hydrates decrease with increasing n, and the difference between them become less than 4 degrees. This behavior may be explained, at least partly, as follows: When n is larger than 3, both the $C_nH_{2n+1}SO_3^-$ anion and the $C_nH_{2n+1}COO^-$ anion can no longer be accommodated in a small cage, like a single pentagonal dodecahedron, because of their increased ionic volume. As a result, they must be accommodated in a larger polyhedron. For such a large polyhedron the distortion of the water network due to the SO_3^- group and COO^- group does not play an important role concerning the stability of the hydrates.

(2) The Formation of Hydrates of Bis(tetrabutylammonium) Alkanedisulfonates and of Bis(tetraisopentylammonium) Alkanedisulfonates. Solid–liquid phase diagrams for the binary systems, water–$[(n\text{-}C_4H_9)_4N]_2[O_3S(CH_2)_nSO_3]$, where n=2—5, are shown in Fig. 4 in the same manner as in Figs. 1 and 2. Three systems with n=2—4 exhibit congruent melting points at concentrations of around X=0.019, indicating that these three salts form a hydrate with hydration numbers of about 52. The melting points of these hydrates, however, are fairly low: they lie between 5.7 and 9.9 °C. The system with n=5 shows two congruent melting points at 1.0 and 1.4 °C at concentrations of around X=0.016 and 0.032, indicating that two kinds of hydrates with hydration numbers of around 61 and 30 are formed. The latter hydrate is also formed by a salt with n=4. In addition, in systems with n=2—4 there are incongruent melting points at concentrations of around X=0.014—0.015; the hydration numbers of the hydrates formed at concentrations below the incongruent compositions seem to be the same as that formed for the n=5 salt, around 61, because of a similarity in the slope ($\partial \log X/\partial(1/T)$) in all systems with n=2—5.

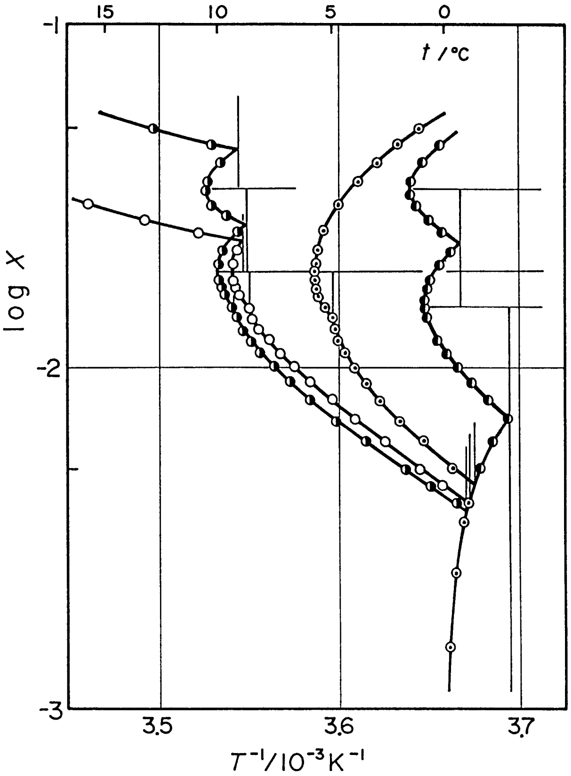

Fig. 4. Solid–liquid phase diagrams for the water–$[(n\text{-}C_4H_9)_4N]_2[O_3S(CH_2)_nSO_3]$ systems. ○: n=2; ⊙: n=3; ◑: n=4; ◐: n=5.

Table 2. Melting Points and Hydration Numbers of the Clathrate-Like Hydrates Formed by a Series of Bis(tetrabutylammonium) Alkanedisulfonates, $[(n\text{-}C_4H_9)_4N]_2[O_3S(CH_2)_nSO_3]$

n	Melting point t_m/°C	Hydration numbers
2	8.7 (incong.)	—
	9.3	52±2
3	5.0 (incong.)	—
	5.7	52±3
4	9.1 (incong.)	—
	9.9	52±2
	10.4	30±2
5	1.0	61±3
	1.4	30±2

All of the melting points, hydration numbers, which are determined from each congruent composition and the congruent melting point, are summarized in Table 2. As mentioned above, three types of hydrates with hydration numbers of around 30, 52, and 61 are formed. The existence of these hydrates has been newly confirmed in this study. No information about the structure of these hydrates is present at this stage. However, hydrates with hydration numbers of about 61 seem to be isostructural with a well-known $(n\text{-}C_4H_9)_4NF\cdot30H_2O$ hydrate,2) since the number of the water molecules per one $(n\text{-}C_4H_9)_4N^+$ cation is almost the same in both hydrates. Although the formation of several types of tetrabutylammonium salt hydrates which have hydration numbers less than 30 per one $(n\text{-}C_4H_9)_4N^+$ cation and fairly high melting points (higher than 10 °C) is known at present,[10] the correlation between these hydrates and those found in this study with hydration numbers of 30 and 52 is uncertain. Another interesting feature of Table 2 is the fact that the melting points of the hydrates of the salt with a short methylene chain of n=2 and with a somewhat long methylene chain of n=4 are higher than those of the n=3 and 5 hydrates. This may be explained by assuming that the n=2 hydrate comprises a sequence of $[(n\text{-}C_4H_9)_4N^+\cdots{}^-O_3S(CH_2)_2SO_3^-]+[(n\text{-}C_4H_9)_4N^+]$, and that the n=4 hydrate $[(n\text{-}C_4H_9)_4N^+\cdots{}^-O_3S(CH_2)_4SO_3^-\cdots(n\text{-}C_4H_9)_4N^+]$ in which the central ${}^-O_3S(CH_2)_4SO_3^-$ anion is surrounded by a large polyhedron made of hydrogen-bonded water networks; in the n=3 hydrate the distortion effect of the ${}^-O_3S(CH_2)_3SO_3^-$ anion on the hydrogen-bonded water network surrounding an $(n\text{-}C_4H_9)_4N^+$ cation will increase compared with that of the ${}^-O_3S(CH_2)_2SO_3^-$ anion in the n=2 hydrate; in the n=5 hydrate the distortion effect of the ${}^-O_3S(CH_2)_5SO_3^-$ anion become larger than that of the ${}^-O_3S(CH_2)_4SO_3^-$ anion in the n=4 hydrate.

The solid–liquid phase diagrams for the binary systems, water–$[(i\text{-}C_5H_{11})_4N]_2[O_3S(CH_2)_nSO_3]$, where n=2—5, are shown in Fig. 5. The phase diagram of the system with n=2 is shown by a broken line because of the similarity of data with those of the n=3 salt. It is clear from this figure that all four systems exhibit congruent melting points at around X=0.013, indicating that these four salts form a hydrate with hydration numbers around 76. Furthermore, the two systems with n=2 and 4 exhibit other congruent melting points around X=0.042—0.043, corresponding to hydrates with hydration numbers of 22—23. All of the melting points and hydration numbers determined are summarized in Table 3, together with some incongruent melting points. These hydrates were newly confirmed in this study. The hydrates with hydration numbers of around 76 seem to be isostructural with a well-known $(i\text{-}C_5H_{11})_4NF\cdot 39H_2O$ hydrate,[3] since the number of water molecules per one $(i\text{-}C_5H_{11})_4N^+$ cation is almost the same in both hydrates. The interesting features of Table 3 are summarized as follows: (1) The melting points of hydrates with hydration numbers of around 76 are 7—12 °C higher than those of the hydrates formed by a series of bis(tetrabutylammonium) alkanedisulfonates (shown in Table 2), suggesting that a hydrogen-bonded framework of water molecules around an $(i\text{-}C_5H_{11})_4N^+$ cation is more stable than that around an $(n\text{-}C_4H_9)_4N^+$ cation, as is often pointed out;[11,18] (2) The order of the melting points with respect to n is 4>2>3>5, which is the same as in the case of bis(tetrabutylammonium) alkanedisulfonate hydrates (shown in Table 2). The reason for this can be explained in the same manner as mentioned above; and (3) For the n=2 and 4 salts hydrates with hydration numbers of 22—23 are slightly stable compared with those of around 76.

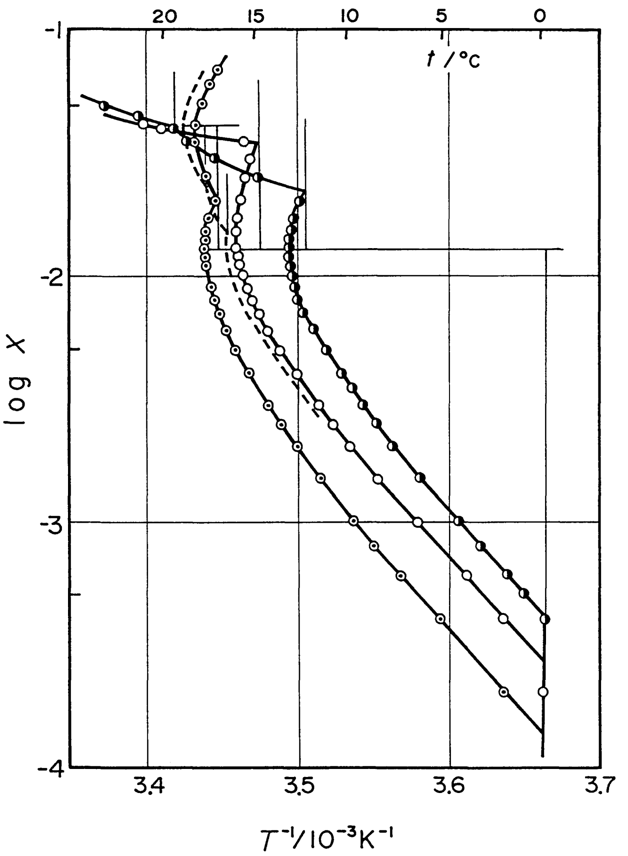

Fig. 5. Solid–liquid phase diagrams for the water–$[(i\text{-}C_5H_{11})_4N]_2[O_3S(CH_2)_nSO_3]$ systems. ○: n=3; ⊙: n=4; ◑: n=5; broken line: n=2.

Finally, in Fig. 6 the melting points of the two series of hydrates of alkanedisulfonates, $[(n\text{-}C_4H_9)_4N]_2[O_3S(CH_2)_nSO_3]$ and $[(i\text{-}C_5H_{11})_4N]_2[O_3S(CH_2)_nSO_3]$, are compared with those of the hydrates of the corresponding alkanedioates,[11] $[(n\text{-}C_4H_9)_4N]_2[OOC(CH_2)_nCOO]$ and $[(i\text{-}C_5H_{11})_4N]_2[OOC(CH_2)_nCOO]$, respectively. The dependence of the melting points on the number of n for the latter two series of hydrates has been discussed in a previous paper.[11] It is obvious from this figure that when the kind of cation is the same, either $(n\text{-}C_4H_9)_4N^+$ or $(i\text{-}C_5H_{11})_4N^+$, the melting points of the alkanedioate hydrates are fairly high compared with those of the alkanedisulfonate hydrates: The melting-

Table 3. Melting Points and Hydration Numbers of the Clathrate-Like Hydrates Formed by a Series of Bis(tetraisopentylammonium) Alkanedisulfonates, $[(i\text{-}C_5H_{11})_4N]_2[O_3S(CH_2)_nSO_3]$

n	Melting point t_m/°C	Hydration numbers
2	16.6	76±4
	17.6 (incong.)	—
	18.9	22±2
3	16.0	76±4
4	17.7	76±3
	18.2	23±2
5	13.1	76±5
	19.6 (incong.)	—

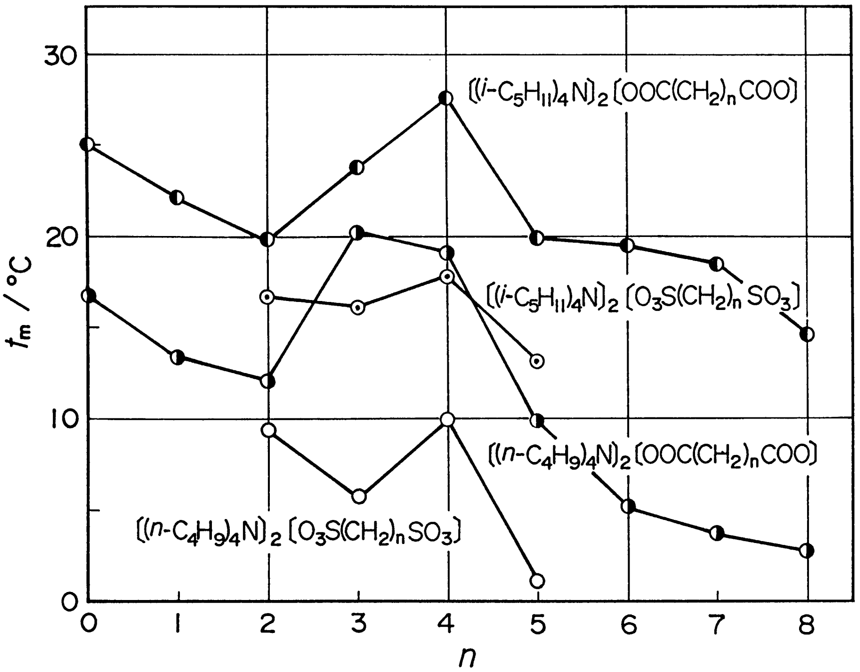

Fig. 6. Relationships between the melting points, t_m, of the hydrates of four series of salts and of the number of carbon atoms, n, of the methylene chain of the anion. ○: $[(n\text{-}C_4H_9)_4N]_2[O_3S(CH_2)_nSO_3]$; ⊙: $[(i\text{-}C_5H_{11})_4N]_2[O_3S(CH_2)_nSO_3]$; ◑: $[(n\text{-}C_4H_9)_4N]_2[OOC(CH_2)_nCOO]$; ◐: $[(i\text{-}C_5H_{11})_4N]_2[OOC(CH_2)_nCOO]$.

point differences are 9—14 °C for the tetrabutylammonium salt hydrates and 7—10 °C for the tetraisopentylammonium salt hydrates for n=3—5, although when n=2 the difference is somewhat slight (about 3 °C) for both hydrates. The high stability of the alkanedioate hydrates probably indicates that a distortion effect of the bulky alkanedisulfonate anion $[O_3S(CH_2)_nSO_3]^{2-}$ on the hydrogen-bonded water networks is larger than that of the alkanedioate anion $[OOC(CH_2)_nCOO]^{2-}$, just as discussed concerning the difference in curves A and C when n=1 and 2 in Fig. 3.

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