Hydrates of Organic Compounds. X. The Formation of Clathrate Hydrates of Tetrabutylammonium Alkanesulfonates

Haruo NAKAYAMA* and Hideyuki USUI
Department of Chemistry, Faculty of Engineering, Yokohama National University,
Tokiwadai, Hodogaya-ku, Yokohama 240

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The solid–liquid phase diagrams of binary mixtures of water with tetrabutylammonium alkanesulfonate ($(n\text{-}C_4H_9)_4NO_3SR(R{=}CH_3\text{–}C_5H_{11})$) and with tetrabutylammonium benzenesulfonate were examined in order to confirm the formation of clathrate-like hydrates. It has been found that (1) all the sulfonates examined can form clathrate-like hydrates with hydration numbers either around 30 or around 39; (2) these hydrates can be classified into three groups I, II, and III on the basis of the hydration numbers and melting points just as in the case of a series of tetrabutylammonium carboxylate hydrates; and (3) generally, the melting points of these sulfonate hydrates are lower than those of tetrabutylammonium carboxylate hydrates. The formation of clathrate-like hydrates of tetrabutylammonium hydrogensulfite and of tetrabutylammonium sulfite has also been reported and is discussed in an appendix.

In previous papers[1,2] the formation of a clathrate-like hydrate by a series of tetrabutylammonium carboxylates ($((n\text{-}C_4H_9)_4NOOCR$; $R{=}H\text{–}C_{10}H_{21}$ and unsaturated alkyl groups ranging from C_2H_3 to C_9H_{17}) was confirmed from the solid-liquid phase diagrams. These hydrates were classified into three groups, I, II, and III, on the basis of the melting points and hydration numbers.

The group I hydrates include the hydrates formed by salts with short alkyl groups such as R=H, CH_3, C_2H_5, $n\text{-}C_3H_7$, $i\text{-}C_3H_7$, $t\text{-}C_4H_9$, C_2H_3(acrylate), and C_3H_5(methacrylate, crotonate, and 3-butenoate). Two characteristic features of the group I hydrates are (a) the hydration number is around 30 and (b) most of the melting points are in the range 10—18 °C, i.e., they are very stable as compared with the group II and III hydrates mentioned below. From the fact that the hydration number is around 30, the crystal structure of the group I hydrates seem to be iso-structural with that of a well-known tetrabutylammonium fluoride hydrate.[3] However, high stability of the group I hydrates cannot be explained by a simple distortion effect of the anion on the hydrogen-bonded water framework within the hydrate.[4] Thus, it has been concluded that the alkyl group of the carboxylate anion is located in a pentagonal dodecahedron, which exists in a gap between the arrangement of large polyhedra (tetrakaidecahedron and/or pentakaidecahedron filled by one of the butyl groups 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.

The group II hydrates are formed exclusively by all the carboxylates with R=C_4H_9, C_5H_{11}, C_4H_7, and C_5H_9 except for $t\text{-}C_4H_9$, and have hydration numbers around 39. The fact that the hydration number is around 39 indicates that the crystal structure of the group II hydrates are essentially similar to those of tetrabutylammonium benzoate hydrate, which has an ideal composition of $(n\text{-}C_4H_9)_4NOOCC_6H_5\cdot 39.5H_2O$,[5] in which the benzoate anion is surrounded by one more large cage of water. The melting points of these hydrates are not so high as those of the group I hydrates; they are at most about 12 °C.

The group III hydrates are formed by tetrabutylammonium carboxylates with long alkyl chains ranging from C_6 to C_{10} including unsaturated chains of C_7 and C_9. Although the hydration number of these hydrates is around 30 as in the case of the group I hydrate, the melting points are appreciably lower than those of the group I hydrates. From the fact that the hydration number is around 30 and such long alkyl chain cannot be accommodated within a single pentagonal dodecahedron, the possible crystal structure of these hydrates will be iso-structural with $(n\text{-}C_4H_9)_4NF$ hydrate but with the long alkyl chain of the carboxylate anion penetrating into two pentagonal dodecahedra which are facesharing with each other. The low stability of these hydrates, i.e., low melting point (around 5 °C or below), can be explained by a large distortion effect caused by the long alkyl chain of the carboxylate anion.

In this paper, from the solid–liquid phase diagrams for eight binary mixtures of tetrabutylammonium alkanesulfonate–water, the effect of the shape and/or length of the alkyl group of a sulfonate anion on the stability and the hydration numbers of their clathrate-like hydrates has been examined from a similar point of view. The formation of clathrate-like hydrates of tetrabutylammonium alkanesulfonates has not been reported previously.

In addition, the formation of clathrate-like hydrates of tetrabutylammonium salts containing either HSO_3^- ion or SO_3^{2-} ion, tetrabutylammonium hydrogensulfite and tetrabutylammonium sulfite, has also been reported and discussed.

Experimental

An aqueous solution of tetrabutylammonium alkanesulfonates, $(n\text{-}C_4H_9)_4NO_3SR$ (R=CH_3, C_2H_5, $n\text{-}C_3H_7$, *i*-

C_3H_7, n-C_4H_9, i-C_4H_9, and n-C_5H_{11}), and of tetrabutylammonium benzenesulfonate was prepared by neutralization of aqueous tetrabutylammonium hydroxide solution with an aqueous solution of either the corresponding alkanesulfonic acid or benzenesulfonic acid. The tetrabutylammonium hydroxide solution was obtained by treating tetrabutylammonium iodide with freshly prepared silver hydroxide in water followed by filtration of the AgI precipitate. Tetrabutylammonium iodide was prepared by precipitation from an aqueous solution of tetrabutylammonium bromide, which was purchased from Tokyo Kasei Kogyo Co. Ltd., with addition of potassium iodide, followed by washing with water and air-drying in a desiccator. The iodide was purified by repeated recrystallization from ethyl acetate–acetone mixture. Methanesulfonic acid and benzenesulfonic acid were purchased from Tokyo Kasei Kogyo Co. Ltd. and ethanesulfonic acid from Aldrich Chemical Co.. These acids were used without further purification. Aqueous solutions of n-$C_3H_7SO_3H$, i-$C_3H_7SO_3H$, n-$C_4H_9SO_3H$, i-$C_4H_9SO_3H$, and n-$C_5H_{11}SO_3H$ 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 2 M† hydrochloric acid solution. The sodium salts, except for n-$C_5H_{11}SO_3Na$ which was purchased from Tokyo Kasei Kogyo Co. Ltd., were synthesized by the Strecker reaction:[6] The corresponding alkyl iodide was refluxed for a few days with an aqueous sodium sulfite solution containing about twice the molar quantity of the iodide. After the water had been evaporated under reduced pressure, the reaction product was extracted with ethanol. The sodium salt was purified by repeated recrystallization from ethanol and was confirmed by its NMR spectra. Differential thermal analyses showed that melting points of all the sodium alkanesulfonates synthesized were higher than 350 °C.

The solid-liquid phase diagrams for the binary systems of water–tetrabutylammonium alkanesulfonate (or tetrabutylammonium benzensulfonate) were determined in the same manner as described in previous papers.[1,4] The concentration of each mother solution of tetrabutylammonium alkanesulfonate was determined by measuring the amount of tetrabutylammonium cation by titration with a sodium tetraphenylborate solution standardized by pure $(n\text{-}C_4H_9)_4NI$ solid.

Results and Discussion

The solid-liquid phase diagrams for tetrabutylammonium alkanesulfonate–water binary systems are shown in Figs. 1 and 2, as well as for a tetrabutylammonium benzenesulfonate–water system. In these figures the logarithm of the concentration of the tetrabutylammonium salt expressed as 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.

In these figures the existence of the congruent melting points at $X \simeq 0.033$ (Figs. 1 and 2) and at $X \simeq 0.024$ (Fig. 2) clearly indicates that these sulfonates can form a clathrate-like hydrate. The former hydrate corresponds to the one with hydration numbers around 30 and the latter around 39. The presence of all the hydrates is confirmed in this study. As is seen in Fig. 2, phase diagrams of tetrabutylammonium 1-propanesulfonate–water and of tetrabutylammonium 1-butanesulfonate–water systems show

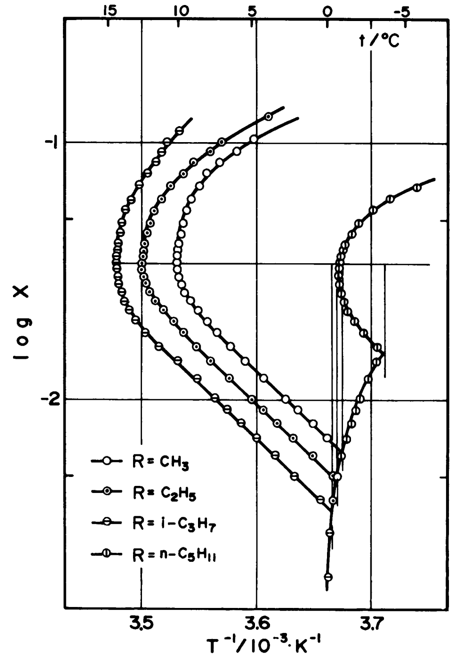

Fig. 1. Solid-liquid phase diagrams for the water–$(n\text{-}C_4H_9)_4NO_3SR$ systems.

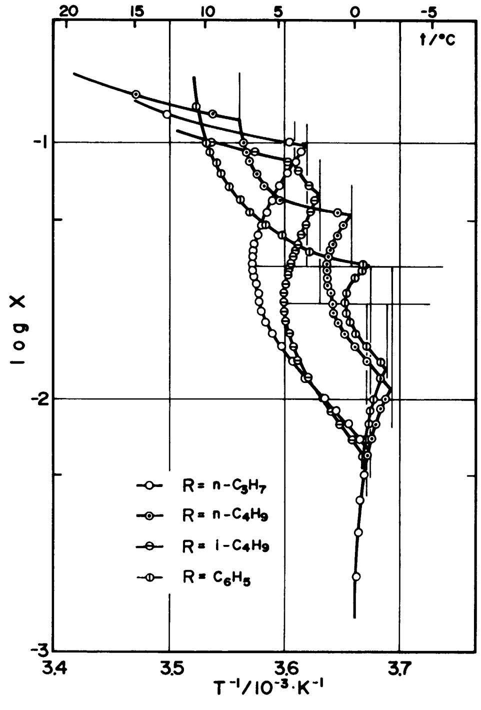

Fig. 2. Solid-liquid phase diagrams for the water–$(n\text{-}C_4H_9)_4NO_3SR$ systems.

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† 1 M=1 mol dm^{-3}.

incongruent melting points at $X \simeq 0.025$. However, this temperature is almost the same as the dissolution temperature of the solution whose concentration is $X=0.024$; i.e., the $\log X$ vs. $1/T$ curve is virtually vertical around $X \simeq 0.024$. For this reason, and also for the other reason mentioned below, it can be concluded that in these systems two kinds of clathrate-like hydrates (with hydration numbers around 30 and 39) are formed simultaneously.

The other reason is the fact that in these two systems the slope $-\partial \log X/\partial(1/T)$ in dilute region, in the vicinity of $X \simeq 0.015$ for example, is about 1.20 times that of the hydrate having hydration numbers around 30 (Fig. 1) and is about 0.9 times that of the tetrabutylammonium 2-methyl-1-propanesulfonate system (Fig. 2) in which only one type of hydrate with hydration number around 39 is formed. It has been concluded in a previous paper[7] that a large portion of the molal heat of solution of a clathrate-like hydrate in water is the molal heat of fusion of the hydrate, which is approximately equal to the molal heat of fusion of ice I multiplied by the hydration number of the hydrate: i.e., the value of the slope $-\partial \log X/\partial(1/T)$ is roughly proportional to the hydration number of the hydrate. Thus, in the two systems noted above the mean hydration number is larger than 30 but smaller than 39. Since the possible structure of the hydrate is either the one with hydration number of around 30 or the one with around 39, this indicates that two types of the hydrates are present simultaneously.

All the melting points and the hydration numbers, determined from each congruent melting point and congruent composition, are summarized in Table 1. Although the curve shown in Figs. 1 and 2 has a fairly flat peak around a congruent composition, the hydration number of each hydrate can be determined within the limits of error indicated in Table 1 since, when the ampoules containing solutions of slightly different composition are warmed gradually, the ampoule which finally dissolves can easily be determined. In Fig. 3, the melting point of the hydrate is plotted against the number of carbon atoms in the main alkyl-chain of each sulfonate anion. The number attached to each point stands for the same sulfonate as the one listed in Table 1. The points corresponding to the hydrates of a series of normal alkanesulfonates are connected by a solid line. A filled circle indicates the hydrate with hydration number around 30 and an open circle indicates the one with a hydration number around 39. Similar to the carboxylate hydrates mentioned above, these hydrates can be classified into three groups; I, II, and III. They are also shown in Fig. 3.

Table 1. Melting Points and Hydration Numbers of a Clathrate-Like Hydrate Formed by a Series of Tetrabutylammonium Alkanesulfonates and Tetrabutylammonium Benzenesulfonate $(n\text{-}C_4H_9)_4NO_3SR$

No	R	Mp θ_m/°C	Hydration number
1	CH_3	10.0	30±1
2	C_2H_5	12.5	30±1
3	$n\text{-}C_3H_7$	6.8	29±2
4*	$n\text{-}C_3H_7$	6.3	39±2
5	$i\text{-}C_3H_7$	14.4	28±2
6	$n\text{-}C_4H_9$	1.8	29±2
7*	$n\text{-}C_4H_9$	1.5	39±2
8	$i\text{-}C_4H_9$	4.6	39±2
9	$n\text{-}C_5H_{11}$	−0.8	30±2
10	C_6H_5	0.6	39±2

* See the text.

The group I hydrates include the hydrates formed by sulfonates with $R=CH_3$, C_2H_5, and $i\text{-}C_3H_7$ (hydrates 1, 2, and 5 in Table 1) and have hydration numbers around 30. As mentioned in the introduction section, it can be concluded that these hydrates are iso-structural with $(n\text{-}C_4H_9)_4NF \cdot 30H_2O$ hydrate and that such alkyl chains as CH_3, C_2H_5, and $i\text{-}C_3H_7$ are accommodated within a vacant pentagonal dodecahedron. These hydrates are fairly stable as compared with the group II and III hydrates mentioned below. The most stable hydrate is that of tetrabutylammonium 3-methyl-1-butanesulfonate (14.4 °C, Table 1), indicating that the group $i\text{-}C_3H_7$ is most suitably fitted to a pentagonal dodecahedron. However, this melting point is relatively lower than that of the most stable carboxylate hydrates of group I: 18.0 °C for $(n\text{-}C_4H_9)_4NOOCC_2H_5$ hydrate.[1]

The group II hydrates which have hydration numbers around 39 are formed by sulfonates with

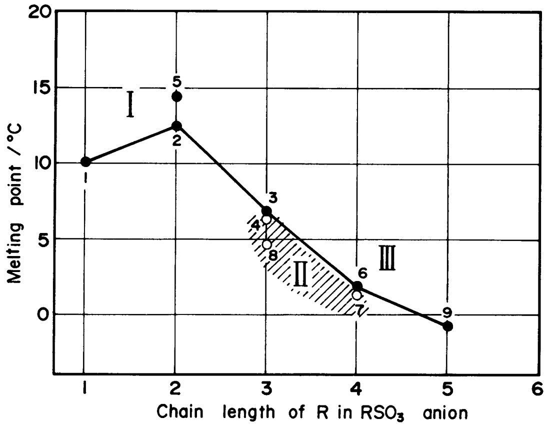

Fig. 3. Relationship between the melting points of the tetrabutylammonium alkanesulfonate, $(n\text{-}C_4H_9)_4NO_3$-SR, hydrates and the chain length of R in the sulfonate anion. The number attached to each point indicates the same hydrate as the one listed in Table 1. Three groups shown by I, II, and III are explained in the text.

R=n-C_3H_7, n-C_4H_9, i-C_4H_9, and C_6H_5 (hydrates 4, 7, 8, and 10 in Table 1). Among them the most stable hydrate is the one with R=n-C_3H_7 (6.3 °C). As mentioned above, in these hydrates such alkyl groups as R=n-C_3H_7, n-C_4H_9, i-C_4H_9, and C_6H_5 seem to be surrounded by either a tetrakaidecahedron or a pentakaidecahedron as in the well-known (n-$C_4H_9)_4NOOCC_6H_5 \cdot 39.5H_2O$[5] hydrate.

Group III hydrates which have hydration numbers around 30, as in the case of the group I hydrates, are fairly unstable and are formed by sulfonates with R=n-C_3H_7, n-C_4H_9, and n-C_5H_{11} (hydrates 3, 6, and 9 in Table 1). These hydrates seem to be iso-structural with the (n-$C_4H_9)_4NF \cdot 30H_2O$ hydrate and such alkyl chains as n-C_3H_7, n-C_4H_9, and n-C_5H_{11} are supposed to be accommodated in a space where two face-sharing pentagonal dodecahedra are present. The hydrates 3 and 6, which have the same anion as the hydrate 4 and 7, respectively, are classified as group III hydrates instead of group I hydrates from the fact that their melting points are relatively low as compared with those of the hydrates 1, 2, and 5. Furthermore such anions as n-$C_3H_7SO_3^-$ and n-$C_4H_9SO_3^-$ are too large to form stable hydrates of group I as is mentioned below (Fig. 4). Although the reason why the sulfonates with R=n-C_3H_7 and n-C_4H_9 can form two kinds of hydrates is not clear; it is obvious that the stability of the two types of hydrates is almost the same since the difference in the melting points between hydrate 3 and 4, and between hydrate 6 and 7, is small as is shown in Table 1.

In Fig. 4 the melting points of a series of tetrabutylammonium alkanesulfonate hydrates are plotted against the conventional partial molal volume ($\overline{V}^\circ_{\mathrm{conv}}$) of the sulfonate anion at 25 °C. This figure includes similar plots for a series of tetrabutylammonium carboxylate hydrates reported earlier.[1] The conventional partial molal anionic volume is defined as a partial molal volume at infinite dilution on the assumption that partial molal volume of H^+ ion at infinite dilution is equal to zero.[14] These are used as an indication of the effective volume of the anion within a hydrate solid since the state in which an anion is surrounded by a hydrogen-bonded water cage will not be so different from the state in which the anion is surrounded by water molecules in an aqueous solution at infinite dilution. The conventional partial molal volume of each carboxylate and alkanesulfonate anion was obtained from the partial molal volume of each sodium salt[8–13] at infinite dilution using the relation that $\overline{V}^\circ_{\mathrm{conv}}$ for Na^+ ion is equal to $-1.21\ \mathrm{cm^3\,mol^{-1}}$ at 25 °C.[14] Since the sulfonate anion is bulky as compared with carboxylate anion, the conventional partial molal volume of $C_nH_{2n+1}SO_3^-$ ion is nearly equal to that of $C_{n+1}H_{2n+3}COO^-$ ion. In Fig. 4, the domains of the group I, II, and III hydrates are also indicated. It is interesting to note that both the stability of the hydrate (i.e., the melting point) and the tendency toward which group of the hydrate can be formed are closely related to the anionic size in the two series of hydrates. However, for the same value of abscissa in Fig. 4 the melting points of a series tetrabutylammonium alkanesulfonate hydrates are lower than those of tetrabutylammonium carboxylate hydrates, indicating that the stability of the hydrates is dependent not only upon the anionic volume but also upon the chemical constitution of the anion. The distortion of the hydrogen-bonded water cage seems to be greater when it surrounds a SO_3 portion than when it surrounds a COO portion, due to the increased number of oxygen atoms in the former structure. The melting point of the tetrabutylammonium benzenesulfonate hydrate, 0.6 °C (Table 1), is also lower than that of tetrabutylammonium benzoate hydrate, which is reported to be about 6.0 °C.[5]

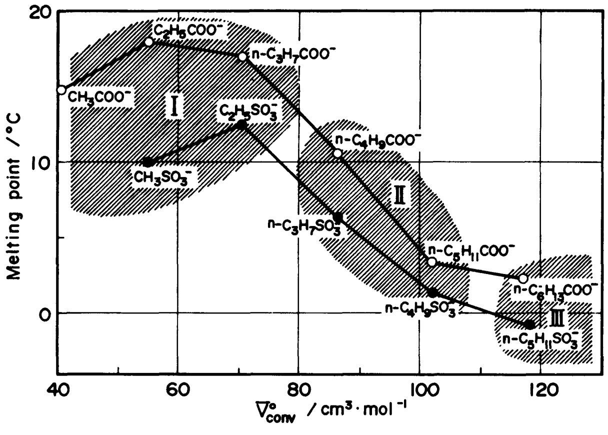

Fig. 4. Relationship between the melting points of the hydrates of either tetrabutylammonium alkanesulfonates or tetrabutylammonium carboxylates and the conventional partial molal anionic volumes. Anions are shown to each point. Three groups shown by I, II, and III are explained in the text.

Appendix

The formation of clathrate-like hydrates of two tetrabutylammonium salts whose anion is either HSO_3^- or SO_3^{2-}, tetrabutylammonium hydrogensulfite ((n-$C_4H_9)_4NHSO_3$) and tetrabutylammonium sulfite ([(n-$C_4H_9)_4N]_2SO_3$), has also been examined, although the electronic structure around the sulfur atom in these inorganic ions is different from that in an alkanesulfonate ion. The solid-liquid phase diagrams of two binary mixtures, (n-$C_4H_9)_4NHSO_3$–H_2O and [(n-$C_4H_9)_4N]_2SO_3$–H_2O, are shown in Fig. 5 in the same manner as in Figs. 1 and 2. Aqueous solutions of these two salts were obtained by neutralization of aqueous (n-$C_4H_9)_4NOH$ solution with an appropriate amount of sulfurous acid solution whose concentration was determined by iodometry.[15] Figure 5 clearly indicates that these

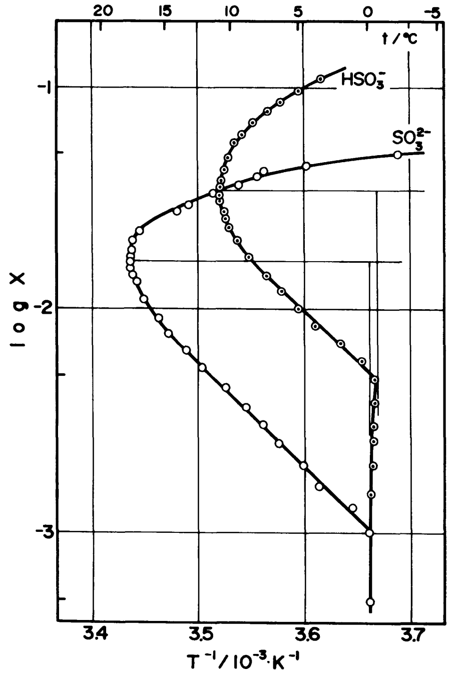

Fig. 5. Solid–liquid phase diagrams for the water–$(n\text{-}C_4H_9)_4NHSO_3$ and water–$[(n\text{-}C_4H_9)_4N]_2SO_3$ systems.

two salts can also form clathrate-like hydrates. This is confirmed in this experiment. The melting point and hydration number are 10.9 °C, 30±2 for the $(n\text{-}C_4H_9)_4NHSO_3$ hydrate and 17.8 °C, 62±4 for the $[(n\text{-}C_4H_9)_4N]_2SO_3$ hydrate, respectively. Like many other clathrate-like hydrates formed by tetrabutylammonium inorganic salts,[4] the crystal structure of both hydrates seems to be iso-structural with the well-known $(n\text{-}C_4H_9)_4NF\cdot 30H_2O$ hydrate since the number of moles of water molecule per $(n\text{-}C_4H_9)_4N^+$ ion is about 30 in both hydrates.

The melting point of the $[(n\text{-}C_4H_9)_4N]_2SO_3$ hydrate is fairly high as has generally been found[4] in other hydrates of tetrabutylammonium salts having di-valent anions like CO_3^{2-} and WO_4^{2-}; 18.3 °C for the carbonate hydrate and 15.0 °C for the tungstate hydrate. The melting point of the $(n\text{-}C_4H_9)_4NHSO_3$ hydrate (10.9 °C) is somewhat higher (about 2 °C) than that expected from a linear relationship between the melting point of the hydrates and $\overline{V}^{\circ}_{conv}$ of anions for a series of hydrates of tetrabutylammonium salts having mono-valent inorganic anions.[4] The value of $\overline{V}^{\circ}_{conv}$ for HSO_3^- ion was estimated to be 25.68 $cm^3\,mol^{-1}$ at 25 °C from a density measurement for an aqueous solution of $NaHSO_3$ in the usual way.[13,16] The slightly elevated melting point of the $(n\text{-}C_4H_9)_4NHSO_3$ hydrate can be ascribed at least partly to the fact that a part of $(n\text{-}C_4H_9)_4NHSO_3$ is converted into $[(n\text{-}C_4H_9)_4N]_2SO_3$, which gives a more stable hydrate than $(n\text{-}C_4H_9)_4NHSO_3$, in aqueous solution since evolution of SO_2 gas is detected when concentrating a dilute solution of $(n\text{-}C_4H_9)_4NHSO_3$ by evaporation of water at reduced pressure. Thus, the aqueous solution of $(n\text{-}C_4H_9)_4NHSO_3$ is somewhat unstable especially in concentrated solution and the hydrate formed from this aqueous solution seems to be a mixed clathrate-like hydrate of $(n\text{-}C_4H_9)_4NHSO_3$ and $[(n\text{-}C_4H_9)_4N]_2SO_3$. Since both hydrates can be considered to be iso-structural with each other as mentioned above, the formation of a mixed clathrate hydrate of both salts is in principle possible. However, the amount of the $[(n\text{-}C_4H_9)_4N]_2SO_3$ salt within the mixed hydrate seems to be small because the observed melting point (10.9 °C) of the hydrate is about 7 °C as low as that of the $[(n\text{-}C_4H_9)_4N]_2SO_3$ hydrate (17.8 °C).

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