Bull. Chem. Soc. Jpn., 56, 877—880 (1983)

Hydrates of Organic Compounds. VII. The Effect of Anions on the Formation of Clathrate Hydrates of Tetrabutylammonium Salts

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(Received September 13, 1982)

Phase diagrams of the binary mixtures of tetrabutylammonium salt $[(n\text{-}C_4H_9)_4N]_nX$ ($X=NO_2$, NO_3, BrO_3, ClO_3, IO_3, ClO_4, MnO_4, and NCS for $n=1$; $X=CO_3$, SO_4, WO_4, and CrO_4 for $n=2$; and $X=PO_4$ for $n=3$) with water were determined over the temperature range between −10 and +50 °C. From these diagrams the following results were obtained: (1) the formation of a clathrate-like hydrate for salts having such anions as NO_2^-, NO_3^-, BrO_3^-, ClO_3^-, IO_3^-, SO_4^{2-}, and PO_4^{3-} was newly confirmed; (2) the melting point of the clathrate hydrate of the salt with monovalent anion was appreciably influenced by the kind of anion; (3) in the hydrates of the salt having either di- or trivalent anions, the melting points were relatively high and were only slightly affected by the kind of anion; (4) the crystal structure of these hydrates was essentially the same as that of the tetrabutylammonium fluoride hydrate, judging from the hydration numbers; (5) the solubilities in water of both permanganate and perchlorate were markedly lower than that of the iodide; and (6) in the thiocyanate system a phase separation into two liquid phases was observed at temperatures higher than +3.5 °C. The effect of a monovalent anion on the stability of the clathrate hydrate was discussed in connection with the conventional partial molal volume of the anion.

Such quaternary ammonium salts as tetrabutylammonium halides[1,2–6] and tetraisopentylammonium halides,[1,2,4–6] are now widely known to form a clathrate-like hydrate, similar to so-called "gas hydrates."[7] In these hydrates, each alkyl group of the quaternary ammonium cation is surrounded by a polyhedron constructed by hydrogen-bonded water molecules. In general, the stability of these quaternary ammonium salt hydrates is affected by two factors: (1) the length and the shape of the alkyl group of the quaternary ammonium cation and (2) the kind of anion. Although the effect of an alkyl group has been extensively investigated in previous papers,[4,5] we have no sufficient data to draw any conclusion as to the influence of an anion on the stability of the hydrate, except that tetrabutyl(or tetraisopentyl)ammonium salts having such anions as F^-, Cl^-, Br^-, HCO_3^-, CrO_4^{2-}, WO_4^{2-}, and HPO_4^{2-} were reported to be able to form stable clathrate hydrates.[1] However, even the existence of some of these hydrates is dubious for the reasons described in the following experimental section.

In this paper, from the phase diagrams for thirteen binary systems consisting of tetrabutylammonium salt–water, the effect of anions on the formation of the clathrate hydrates has been examined. The information about what kind of anion can contribute to the formation of the clathrate hydrate and to what extent the melting point of the hydrate is affected by the kind of anion will be of great value for an application of these hydrates, for example, (1) as a heat reservoir utilizing the heat evolved or absorbed when their states change and (2) for highly selective separation of a specific anion from an aqueous solution containing several kinds of anions through the formation of a mixed clathrate hydrate.[8]

Experimental

Materials. Aqueous solutions of the tetrabutylammonium salts, except for perchlorate and permanganate, were prepared by reaction between tetrabutylammonium iodide and the corresponding silver salt in water, followed by filtration of AgI precipitate. Tetrabutylammonium iodide was synthesized by reacting tributylamine with butyl iodide in ethyl acetate and was purified by recrystallization from ethyl acetate–acetone mixture. Such silver salts as $AgNO_3$, $AgClO_3$, $AgIO_3$, Ag_2WO_4, Ag_2SO_4, and Ag_2CrO_4 were purchased from Tokyo Kasei Kogyo Co. Ltd. and were used without further purification. The other silver salts, like $AgNO_2$, AgNCS, $AgBrO_3$, Ag_2CO_3, and Ag_3PO_4, were prepared by mixing an aqueous solution of $AgNO_3$ with the corresponding sodium salt solution. These slightly soluble salts were filtered off, washed with cold water, and used in a wet state.

We attempted and failed to prepare such silver salts as $AgHCO_3$, $AgHSO_4$, AgH_2PO_4, and Ag_2HPO_4. When a sodium hydrogencarbonate solution was mixed with a silver nitrate solution, a yellowish white solid was precipitated with evolution of gas, which was presumably carbon dioxide, indicating that the solid was Ag_2CO_3 rather than $AgHCO_3$. The X-ray diffraction pattern of the solid thus obtained was exactly the same as that of Ag_2CO_3 (ASTM 12-766). The white precipitate obtained from the reaction of a silver nitrate solution and a $NaHSO_4$ solution was also believed to be Ag_2SO_4 instead of $AgHSO_4$, since a supernatant solution became highly acidic, indicating a liberation of hydrogen ion, and the X-ray diffraction pattern of the solid thus obtained gave a similar pattern to that of Ag_2SO_4 (ASTM 7-203) although the diffraction intensities corresponding to $l=3$ were relatively low as compared to those of Ag_2SO_4. Similarly, the yellow solid which was formed by mixing a silver nitrate solution with either a NaH_2PO_4 or a Na_2HPO_4 solution was also concluded to be Ag_3PO_4 from the following reasons: (1) a supernatant solution became highly acidic (pH ≈2.5) and the amount of a NaOH solution required to neutralize the supernatant solution agreed very closely with that calculated on the assumption that all the hydrogen, which was initially contained in each phosphate ion, was completely dissociated into hydrogen ion in the supernatant mixture; (2) when an excess amount of $AgNO_3$ solution was reacted with a known amount of each phosphate solution (NaH_2PO_4 or Na_2HPO_4), the silver ion content remaining in the supernatant mixture was reasonably explained by assuming that the precipitate was Ag_3PO_4 in both cases; and (3) their X-ray diffraction patterns were exactly the same as that of Ag_3PO_4 (ASTM 6-505).

Therefore, the existence of hydrates of $(n\text{-}C_4H_9)_4NHCO_3$

and of $[(n\text{-}C_4H_9)_4N]_2HPO_4$, reported by McMullan and Jeffrey,[1] is dubious since they reported that these salts were prepared by a reaction of tetrabutylammonium iodide with the corresponding silver salts.

Tetrabutylammonium perchlorate was prepared by mixing a tetrabutylammonium bromide solution with an aqueous $NaClO_4$ solution, and purified by recrystallization from water. Tetrabutylammonium permanganate was prepared by mixing a tetrabutylammonium chloride solution with a $KMnO_4$ solution, followed by filtration of the mixture and washing it with cold water.

Measurements and Analyses. Phase diagrams for the binary systems of water–tetrabutylammonium salt, except for perchlorate, permanganate and thiocyanate, were determined in the same manner as described in the previous paper[5] (an ampoule method). The concentrations of mother solutions were mostly determined by measuring the water content using the Karl Fischer titration method on a MK-AII apparatus (Kyoto Electronics Manufacturing Co.). For mother solutions containing anions which interfered with the Karl Fischer titration method, the concentrations were determined by one of the following methods: (1) titration by a standard sodium tetraphenylborate solution for the nitrite and iodate solutions; (2) titration by 0.1 mol dm^{-3} hydrochloric acid solution for the carbonate solution; and (3) ordinary iodometry[9] for the chromate solution. The titration method using a sodium tetraphenylborate was carried out in the following way. A sample containing about 1×10^{-4} equivalent was diluted with water to about 15 cm^3. After addition of 0.5 cm^3 of 0.05 wt% Bromophenol Blue solution (indicator), 10 cm^3 of chloroform and 10 cm^3 of 0.1 mol dm^{-3} NaOH solution in this order, the whole mixture was stirred vigorously with a magnetic stirrer for about 15 m. Then the solution was titrated with a 0.02 M $(C_6H_5)_4BNa$ solution, which had been standardized with a known amount of pure $(n\text{-}C_4H_9)_4NI$, until the color in the lower chloroform phase changed from blue to colorless.

The phase diagrams of the systems containing such sparingly soluble salts as perchlorate and permanganate were determined by measuring the solubility of each solid in water at various temperatures.[5] The concentration of perchlorate solution was determined gravimetrically after evaporating a known amount of the solution to dryness at 50 °C under reduced pressure. The concentration of permanganate solution was determined by a standard iodometric method.[9] The phase diagram of the thiocyanate system, in which a liquid-liquid phase separation occurred, was determined by measuring the respective concentrations of the two liquid phases which were in equilibrium with each other at a given temperature. The concentration determination of thiocyanate ion was carried out by a standard KNCS titration method (the Volhard method).[9]

Results and Discussion

(1) Clathrate Hydrate Formation of Tetrabutylammonium Salts Having Monovalent Anions. The solid-liquid phase diagrams for the binary systems, water–$(n\text{-}C_4H_9)_4NX$, where X=NO_2, NO_3, ClO_3, BrO_3, and IO_3, are shown in Fig. 1. 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 the figure. For comparison, Fig. 1 includes the phase diagram of the tetrabutylammonium fluoride–water system reported earlier.[5]

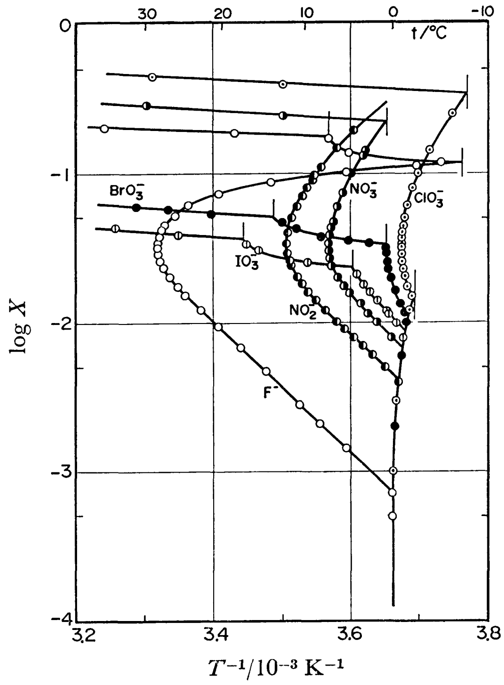

Fig. 1. Solid-liquid phase diagrams for the water–$(n\text{-}C_4H_9)_4NX$ systems.
○: X=F, ◐: X=NO_2, ◑: X=NO_3, ●: X=BrO_3, ⊙: X=ClO_3, ⦶: X=IO_3.

TABLE 1. MELTING POINTS AND HYDRATION NUMBERS OF TETRABUTYLAMMONIUM SALT CLATHRATE HYDRATES

Anion	Mp θ_m/°C	Hydration number
F^-	28.3[5,6]	30±1[5,6]
NO_2^-	11.5	29±2
NO_3^-	7.3	30±1
ClO_3^-	−0.9	30±2
BrO_3^-	0.8 (incongruent)	—
IO_3^-	4.9 (incongruent)	—
CO_3^{2-}	18.3	66±2
SO_4^{2-}	12.6	64±2
CrO_4^{2-}	12.7 (13.6[1])	66±2 (65—68[1])
WO_4^{2-}	15.0 (15.1[1])	64±2 (60—63[1])
PO_4^{3-}	17.8	100±4

Figure 1 clearly shows that the three salts with X=NO_2, NO_3, and ClO_3 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. The congruent compositions of these three hydrates are almost the same as that of the fluoride hydrate. This suggests that these newly found hydrates have the same crystal structure as that of the fluoride hydrate.[3] The melting points and the hydration numbers calculated from their congruent compositions are summarized in Table 1, together with those previously reported.[4–6]

The phase diagrams for the bromate and iodate systems resemble each other and are different from those of the other salts. They show the existence of three types of solid phases other than ice over the temperature range studied. The incongruent melting points and corresponding compositions are 0.8 °C, X=0.032 and 14.0 °C, X=0.050 for the bromate and 4.9 °C, X=0.024 and 17.3 °C, X=0.034 for the iodate, respectively. Of these phases, the ones which are stable over a low temperature interval of −2.1—+0.8 °C for the bromate and of −1.5—4.9 °C for the iodate seem to be clathrate hydrates, since not only the temperature dependence of the solubility curves of these two phases but also their morphological appearance is quite similar to those of the other clathrate hydrates. The incongruent melting points of the two hydrates are also given in Table 1. As is obvious from Fig. 1, these incongruent melting points are very close to their hypothetical congruent melting points since the incongruent composition is comparable to that of the hydrate itself ($X \simeq 0.033$).

As pointed out above, the melting points of these hydrates are considerably lower than that of, for example, the fluoride hydrate,[4-6] indicating that the hydrogen-bonded water lattice within the hydrate solid is markedly distorted by the presence of the anion, which is polyatomic and consequently more bulky than a simple anion such as a fluoride ion. Generally, it is hardly possible to evaluate quantitatively the effect of anions on the lattice distortion, because of the lack of any precise knowledge about the behavior of anions within the lattice, for example, about the possibility of hydrogen-bond formation between an oxygen atom of the anion and a hydrogen atom of the water molecule included in the lattice. Here we simply discuss the effect of the geometrical size of an anion on the lattice distortion of the hydrate from the following point of view. Firstly, as an estimation of the effective size of an anion within the hydrate crystal, it would be appropriate to refer to an ionic volume in an aqueous solution rather than its intrinsic (crystallographic) volume, since the anion present in the hydrate solid is undoubtedly surrounded by many water molecules, as if it were in an aqueous solution. Secondly, the ionic volume in an aqueous solution which we can use quantitatively is a conventional partial molal ionic volume at infinite dilution, $\bar{V}^\circ_{\text{conv}}$, based on the assumption that the partial molar volume of hydrogen ion at infinite dilution is 0 cm^3/mol.[10]

In Fig. 2 the melting point of each hydrate, which may be considered an indication of the stability of the hydrate, is tentatively plotted against the $\bar{V}^\circ_{\text{conv}}$ of the respective anions at 25 °C including halide and hydroxide hydrates already reported.[11] The melting points of both iodate and bromate hydrates are estimated from the temperature dependence of their solubility curves, which are shown in Fig. 1. It is obvious from this figure that the melting point of the hydrate decreases almost linearly with increasing the $\bar{V}^\circ_{\text{conv}}$, indicating that the stability of the hydrate is to a considerable extent governed by the distortion effect of the anion. The relationship found in Fig. 2 could also be used to estimate the melting point of the hydrate of tetrabutylammonium salt having a monovalent anion not examined in this study. It is interesting to note that Fig. 2 can reasonably explain the fact that tetrabutylammonium salts having large anions[10] such as I^- ($\bar{V}^\circ_{\text{conv}}$=36.22 cm^3/mol), NCS$^-$($\bar{V}^\circ_{\text{conv}}$=35.7 cm^3/mol), MnO$_4^-$($\bar{V}^\circ_{\text{conv}}$=42.5 cm^3/mol) and ClO$_4^-$ ($\bar{V}^\circ_{\text{conv}}$=44.12 cm^3/mol) cannot form stable clathrate hydrates.

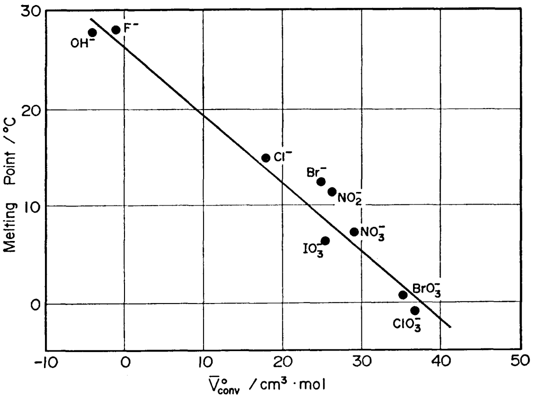

Fig. 2. Relationship between the melting points and the conventional partial molal anionic volumes in the clathrate hydrates of tetrabutylammonium salts with monovalent anions.

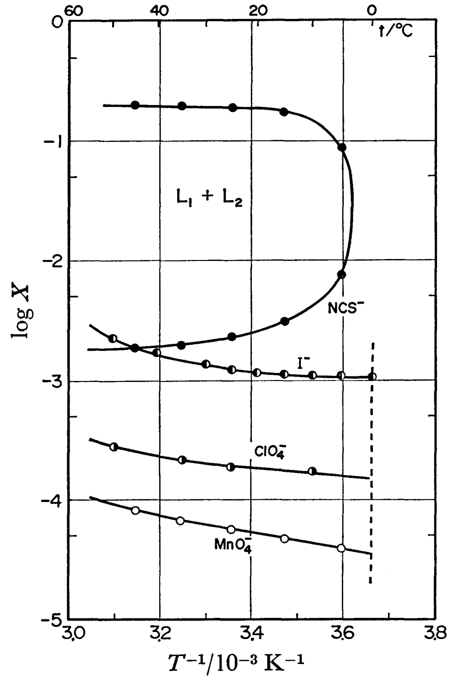

Fig. 3. Solid-liquid and liquid-liquid phase diagrams for the water–$(n\text{-}C_4H_9)_4NX$ systems.
◐: X=I, ○: X=MnO$_4$, ◑: X=ClO$_4$, ●: X=NCS.

The phase diagrams for systems which do not form hydrates are shown in Fig. 3 in the same way as in Fig. 1. This figure includes the phase diagram of the water–$(n\text{-}C_4H_9)_4NI$ system[5] for comparison. The characteristics of this figure are summarized as follows: (1) the solubilities in water of both permanganate and perchlorate are considerably lower than that of the iodide, which is well known to be a sparingly soluble salt (for example, at 25 °C, the solubilities are 0.112 wt%, 0.345 wt%, and 2.447 wt%[5] for permanganate, perchlorate, and iodide, respectively); and (2) a phase separation into two liquid phases occurs in the thiocyanate system with lower critical solution temperature of +3.5 °C.

(2) Clathrate Hydrate Formation of Tetrabutylammonium Salts Having Di- and Trivalent Anions. The solid-liquid phase diagrams for the binary systems, water–$[(n\text{-}C_4H_9)_4N]_2Y$, where Y=$CO_3$, SO_4, WO_4, and CrO_4, and water–$[(n\text{-}C_4H_9)_4N]_3PO_4$, are shown in Fig. 4. This figure clearly shows that all the salts studied can form clathrate hydrates which melt congruently. Their melting points and hydration numbers are also listed in Table 1. Of these hydrates, the carbonate, sulfate, and phosphate hydrates are newly confirmed in this study. The data for both chromate and tungstate hydrates are in good agreement with those reported earlier,$^{1)}$ although some discrepancy in the melting point of the chromate hydrate is seen.

It is interesting to note that these hydrates are fairly stable, as compared with those of the salts with monovalent anion mentioned in the previous section. This fact indicates that the distortion effect of the anion on the water lattice within the hydrate crystal is relatively small. One reason for this will be the fact that the number of anion per one $(n\text{-}C_4H_9)_4N^+$ cation is reduced to either a half or a third of the above mentioned case. An approximately linear relationship between the melting point and the $\bar{V}^\circ_{\text{conv}}$ of anion, found for the salts with monovalent anion (Fig. 2), cannot be seen in this series of hydrates, since their melting points vary only over a limited range of temperature (13—18 °C), whereas the $\bar{V}^\circ_{\text{conv}}$'s widely vary from $-4.3\ \text{cm}^3/\text{mol}^{10)}$ for CO_3^{2-} ion to $25.7\ \text{cm}^3/\text{mol}^{10)}$ for WO_4^{2-} ion. This suggests that the distortion on the water lattice due to the introduction of divalent (or trivalent) anion is not the dominant factor which determines the stability of the hydrate. The slight difference in stability of these hydrates seems to be governed by such factors as either geometrical shape of the anion or slight difference in the ability of hydrogen-bond formation of the oxygen atom of the anion with a water molecule.

Judging from the hydration numbers listed in Table 1, the crystallographic structure of these hydrates is believed to be essentially the same as that of the salts with monovalent anion since the numbers of water molecules per one $(n\text{-}C_4H_9)_4N^+$ cation are approximately equal. The fact that the number of water molecules per one $(n\text{-}C_4H_9)_4N^+$ cation in the hydrates of salts with either di- or trivalent anions, around 33, is slightly larger than 30 found in the series of salts with monovalent anion, will be reasonable since the number of water molecules which construct the clathrate lattice must increase in order to fill the vacant space arising from the decrease in the number of anions.

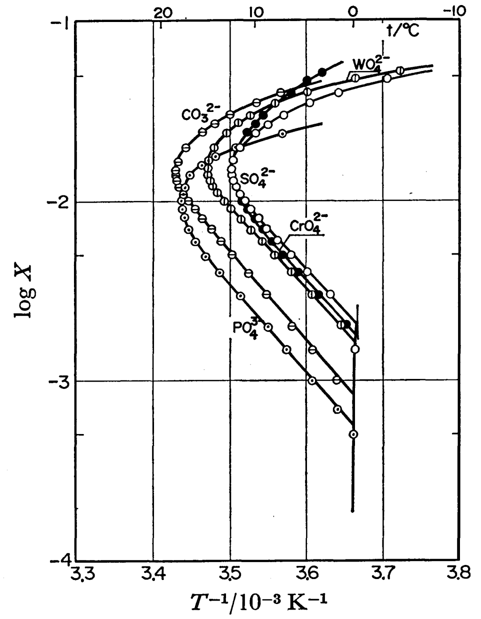

Fig. 4. Solid-liquid phase diagrams for the water–$[(n\text{-}C_4H_9)_4N]_2Y$ and water–$[(n\text{-}C_4H_9)_4N]_3PO_4$ (⊙) systems.
⊖: Y=CO_3, ○: Y=SO_4, ●: Y=CrO_4, ⦶: Y=WO_4.

The present work was supported by the Asahi Glass Foundation for Industrial Technology and by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture No. 57540240.

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