Bull. Chem. Soc. Jpn., 54, 3717—3722 (1981)

Solid-Liquid and Liquid-Liquid Phase Equilibria in the Symmetrical Tetraalkylammonium Halide-Water Systems

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(Received May 11, 1981)

Solid-liquid and liquid-liquid phase diagrams of the binary R_4NX–water ($R=n\text{-}C_3H_7$—$n\text{-}C_6H_{13}$ and $i\text{-}C_5H_{11}$; X=F, Cl, Br, and I) systems were determined in the temperature range between −20 °C and +80 °C. These diagrams showed (1) the formation of a clathrate-like hydrate for four salts $(n\text{-}C_5H_{11})_4NF$, $(n\text{-}C_5H_{11})_4NCl$, $(i\text{-}C_5H_{11})_4NBr$, and $(i\text{-}C_5H_{11})_4NI$; (2) a phase separation into two liquid phases in the systems of $(n\text{-}C_5H_{11})_4NBr$, $(i\text{-}C_5H_{11})_4NBr$, $(n\text{-}C_6H_{13})_4NCl$, and $(n\text{-}C_6H_{13})_4NBr$; (3) that the solubility (in water at a definite temperature) of a series of the salts did not show a systematic change with respect to either the alkyl-chain length or the kind of anion; and (4) that the salt which gave the maximum solubility in water at 25 °C was $(n\text{-}C_5H_{11})_4NCl$ for chloride, $(n\text{-}C_4H_9)_4NBr$ for bromide, and $(C_2H_5)_4NI$ for iodide, respectively. The effect of anions on the solubilities of a series of salts having the same cation was examined. It was found that the ratio m_{Cl}/m_I at 25 °C became as high as 22800 for the tetrapentylammonium salts. Phase diagrams for the bolaform salt $[(n\text{-}C_4H_9)_3N(CH_2)_6N(n\text{-}C_4H_9)_3]X_2$–water systems are also presented.

Though it is well known that the solubilities of symmetrical tetraalkylammonium halides in water are generally high except for iodides, accurate numerical values have been reported only for a limited number of salts[1] and even among the existing data some discrepancies are seen. Our studies on the formation of clathrate hydrates of quaternary ammonium halides[2–4] have found that the solubilities of these salts in water depend sensitively on the temperature, since the phenomena such as the formation of clathrate hydrate and/or the phase separation into two liquids are often observed.

Thus, it would be important to know an accurate phase diagram for the binary mixture of these salts with water before various properties of its aqueous solution are examined. So far as the author knows, no complete phase diagrams for the symmetrical tetraalkylammonium halide–water systems have so far been examined, except for tetrabutylammonium bromide,[5] tetrabutylammonium iodide,[6] and tetrapentylammonium iodide.[6] For the latter two iodides the solubilities in water have been measured at various temperatures (2—43 °C). In this paper we are reporting the complete phase diagrams of the R_4NX ($R=n\text{-}C_3H_7$, $n\text{-}C_4H_9$, $n\text{-}C_5H_{11}$, $i\text{-}C_5H_{11}$, and $n\text{-}C_6H_{13}$; X=F, Cl, Br, and I)–water systems, together with those of the $[(n\text{-}C_4H_9)_3N(CH_2)_6N(n\text{-}C_4H_9)_3]X_2$–water systems.

Experimental

Materials. All the iodides R_4NI ($R=n\text{-}C_3H_7$, $n\text{-}C_4H_9$, $n\text{-}C_5H_{11}$, $i\text{-}C_5H_{11}$, and $n\text{-}C_6H_{13}$) were synthesized by reacting trialkylamines with the corresponding alkyl iodide in ethyl acetate and were purified by recrystallization either from ethyl acetate or ethyl acetate–acetone mixture.[2] These iodides were confirmed by their NMR spectra. Other halides were obtained by neutralizing each hydroxide solution with its corresponding acid HX (X=F, Cl, or Br). The hydroxide solution was prepared by reacting iodide with freshly prepared silver hydroxide in water with vigorous shaking, followed by filtration in a CO_2-free atomsphere.[3] A series of salts $(n\text{-}C_4H_9)_4NX$ and $(i\text{-}C_5H_{11})_4NX$ (X=F, Cl, and Br) was purified by separating out the solids in the form of clathrate hydrates from the above neutralized solutions by cooling. Anhydrous $(n\text{-}C_5H_{11})_4NBr$ was purified by recrystallization from water. Other salts could not be purified either because of high solubility in water or because of two-liquid phase separation. It was observed that three fluorides $(n\text{-}C_4H_9)_4NF$, $(n\text{-}C_5H_{11})_4NF$, and $(n\text{-}C_6H_{13})_4NF$ gradually decomposed when their aqueous solutions were concentrated by evaporation of water. Melting points are summarized in Table 1. Figures in parentheses represent the water content (wt%) of the sample. These salts are somewhat hygroscopic.

Table 1. Melting points (°C) of symmetrical tetraalkylammonium halides R_4NX

R	X		
	Cl	Br	I
$n\text{-}C_3H_7$	143—145(1.6)[a]	293—295(0.1)	>290(0.1)
$n\text{-}C_4H_9$	70—74(3.5)	99—100(0.9)	145—147(0.1)
$n\text{-}C_5H_{11}$	—	99—100(1.1)	134—135(0.2)
$i\text{-}C_5H_{11}$	67—68(1.5)	131—132(0.7)	146—147(0.1)
$n\text{-}C_6H_{13}$	—	81—83(5.3)	103—104(0.8)

a) Figures in parentheses represent the water content (wt%).

Measurements and Analyses. Phase diagrams for the systems containing all the fluorides and the salts R_4NX having $R=n\text{-}C_3H_7$, $n\text{-}C_4H_9$, $i\text{-}C_5H_{11}$ and X=Cl and Br were determined in the following manner. A sample solution (about 1.0—1.5 g) was prepared by weighing out water and a concentrated mother solution; it then was sealed in a small glass ampoule. The concentrations of the mother solutions were determined either by measuring the water content using the Karl Fischer titration method on a MK-AII apparatus (Kyoto Electronics Manufacturing Co.) or by a standard KNCS titration method (the Volhard method).[7]

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 dissolved. After that, the ampoule was slowly warmed (at the rate of about 0.5 °C per hour) with vigorous shaking in a constant temperature bath and the temperature at which the solid phase completely disappeared was accurately determined.

All the phase diagrams of the iodide–water systems were determined by measuring their solubilities in water at various temperatures. In a measuring cell (3 cm diameter and 10 cm high) immersed in a constant temperature bath, the iodide solid was saturated in 10—20 cm^3 of water by vigorous mixing with a magnetic stirrer for 2—10 h. Then a given amount of each saturated solution was withdrawn and was analyzed by the KNCS titration method.

The phase diagrams of $(n\text{-C}_5\text{H}_{11})_4\text{NBr}$, $(n\text{-C}_6\text{H}_{13})_4\text{NCl}$, and $(n\text{-C}_6\text{H}_{13})_4\text{NBr}$ systems, in which a liquid-liquid phase separation occurred, were determined either by an ampoule method or by a solubility measurement. In the former method, the temperature at which the phase separation occurred was measured when an aqueous solution, sealed in an ampoule, was gradually heated. In the latter method, the respective concentrations of the two liquid phases which were in equilibrium with each other at a given temperature were determined by the KNCS titration method.

Results

Tetrapropylammonium Halide–Water Systems. Figure 1 shows the phase diagrams of the tetrapropylammonium halide–water systems. The logarithm of the concentration expressed in mole fraction (X) is plotted against the reciprocal of the absolute temperature. For comparison, the temperature expressed in ordinary Celsius scale is shown on the upper side of the figure. This figure indicates a typical behavior of symmetrical lower quaternary ammonium salts; high solubilities for fluoride, chloride, and bromide and relatively low solubility for iodide. At 25 °C, for example, X's of the chloride and the bromide were 0.255 and 0.162, which correspond to 80.8 and 74.1 wt%, respectively. On the other hand, X was only 0.011 (16.2 wt%) for iodide, though this iodide was the most soluble among the iodides investigated in this study.

In the concentration range between X=0.05 and 0.15, no solid phase appeared, except for the iodide, from the solutions which were kept at −30 °C for two months. Thus, the phase diagrams in this region remain uncertain.

Tetrabutylammonium Halide–Water Systems. The solid-liquid phase diagrams for $(n\text{-C}_4\text{H}_9)_4\text{NX}$–water systems are shown in Fig. 2 in the same manner as in Fig. 1. The phase diagram for the bromide is in fairly good agreement with the one reported by Diadin *et al.*[5] At temperatures higher than about 30 °C, these phase diagrams also exhibit a similar trend to that in Fig. 1; low solubility for the iodide and high solubilities for the other salts. However, at lower temperatures, the phase diagrams, except for that of iodide, become fairly complicated because of the formation of clathrate-like hydrates[2,5,8,9] and other lower hydrates. The congruent melting point and its composition is 28.3 °C, X=0.032 for the fluoride, 15.0 °C, X=0.032 for the chloride, and 12.9 °C, X=0.040 for the bromide, respectively. These X values correspond to the hydrates $(n\text{-C}_4\text{H}_9)_4\text{NF}\cdot 30\text{H}_2\text{O}$, $(n\text{-C}_4\text{H}_9)_4\text{NCl}\cdot 30\text{H}_2\text{O}$, and $(n\text{-C}_4\text{H}_9)_4\text{NBr}\cdot 24\text{H}_2\text{O}$. For the bromide hydrate two more incongruent melting points were recognized at 9.8 °C (X=0.0168) and at 12.4 °C (X=0.033), although the composition of each hydrate is not known. Diadin *et al.*[5] have reported three incongruent melting points at 9.5, 11.6—11.7, and 12.2 °C and a congruent melting point at 12.36 °C which is slightly different from our result (12.9 °C). A slight discrepancy in a melting point of a clathrate hydrate is often observed.[10,11]

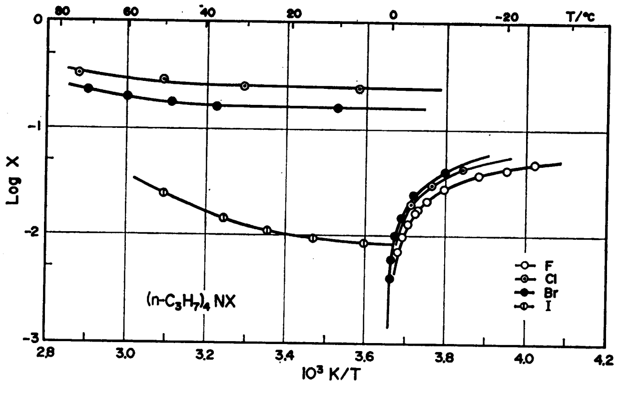

Fig. 1. Solid-liquid phase diagrams for the tetrapropylammonium halide-water systems.

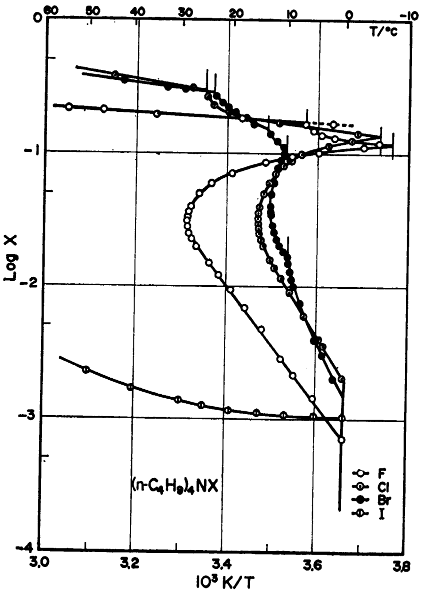

Fig. 2. Solid-liquid phase diagrams for the tetrabutylammonium halide–water systems.

It is interesting to note that the composition of the eutectic points of the clathrate hydrate–ice system are very low (X=0.00075 for the fluoride, 0.0019 for the chloride, and 0.0014 for the bromide). This means that the solubilities of these salts are quite low at temperatures slightly higher than the eutectic point and steeply increase with increasing temperature.

The composition of the other solid phases formed in the concentration ranges of X=0.118—0.168 for the fluoride, X=0.134—0.282 for the chloride, and X= 0.106—0.275 for the bromide were not known because the solutions in this concentration ranges, which were highly viscous, were supercooled so easily that ordinary thermal analysis could not be applied. Diadin *et al.*[5] have reported two solid phases $(n\text{-C}_4\text{H}_9)_4\text{NBr}\cdot 3\text{H}_2\text{O}$ and $(n\text{-C}_4\text{H}_9)_4\text{NBr}\cdot 2\text{H}_2\text{O}$.

The solubility of the iodide is about 10 per cent higher than that reported by Franks and Clarke[6] over the temperature range examined and the minimum in the $\log X$ *vs.* T^{-1} curve exists near at 5 °C instead of 12.6 °C.[6]

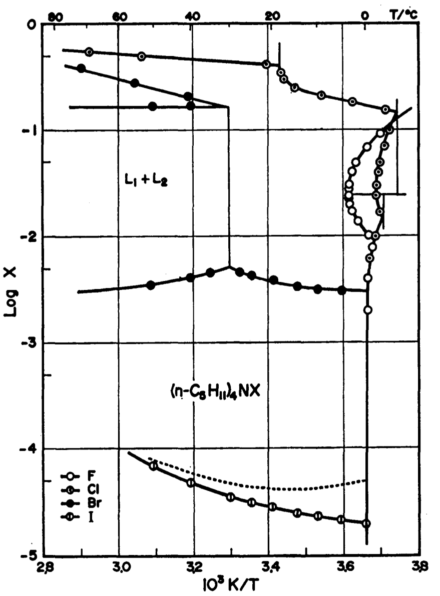

Fig. 3. Solid-liquid and liquid-liquid phase diagrams for the tetrapentylammonium halide–water systems.
Dotted line indicates the solubility data for the iodide taken from the Ref. 6.

Tetrapentylammonium Halide–Water Systems. The solid-liquid and liquid-liquid phase diagrams for the $(n\text{-}C_5H_{11})_4NX$–water systems are shown in Fig. 3. For the fluoride and chloride systems, there exist fairly unstable congruent melting points (3.6 °C and −2.3 °C) indicating the formation of clathrate-like hydrates. The peak composition of both hydrates lies around $X=0.025$, which corresponds to a hydrate of hydration number 39. The formation of clathrate hydrates of tetrapentylammonium salts has not been reported so far. It is interesting to note that three fairly unstable hydrates can only be formed in the narrowly-limited concentration range of $X\simeq0.01$—0.1, in striking contrast to the case of tetrabutylammonium (Fig. 2) and tetraisopentylammonium (given later, Fig. 4) salt hydrates.

In the bromide system, phase separation into two liquids occurs above 30.4 °C. The concentration of both phases were, at 50 °C for example, 6.78 wt% in the water-rich phase and 80.92 wt% in the salt-rich phase. Below 30.4 °C the solid phase, which seems to be anhydrous, is in equilibrium with a relatively dilute solution of about 8 wt% or less. This indicates that the solubility of the bromide below 30.4 °C is about a hundredth of that of the chloride.

The solid-liquid equilibrium curve for the iodide is not in agreement with that reported by Franks and Clarke;[6] their curve is shown in Fig. 3 by a dotted line. The observed solubilities were about 1.4 times lower at 25 °C and about 2 times lower at 5 °C than the reported values. Furthermore, our data did not show the existence of a minimum around 16 °C.[6]

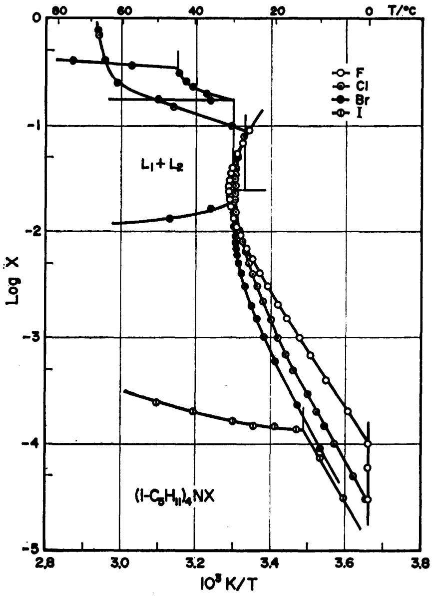

Fig. 4. Solid-liquid and liquid-liquid phase diagrams for the tetraisopentylammonium halide–water systems.

Tetraisopentylammonium Halide–Water Systems. The phase diagrams for the tetraisopentylammonium halide–water systems are given in Fig. 4. The striking feature in this figure is that the formation of clathrate hydrates occurs over a very wide concentration range. In the fluoride system, clathrate hydrate occurs from solutions greater than $X=1\times10^{-4}$ (0.176 wt%), and the solubility of the hydrate steeply increases with increasing temperature. The congruent melting point of the hydrate is 31.5 °C and its X is 0.025, which corresponds to the hydration number of 39. These values are in fairly good agreement with those reported earlier (31.2 °C and about 40).[9] The phase diagrams in the concentrated regions are somewhat uncertain because a solution more concentrated than about $X=0.1$ (66 wt%) gradually decomposes even at room temperature.

The phase diagram of the chloride system exhibits almost the same behavior as that of the fluoride. The formation of clathrate hydrate begins from a solution as low as $X=3\times10^{-5}$ (0.0556 wt%). The melting point and the composition of the hydrate is 29.6 °C and $X=0.025$, which corresponds to the same hydration number 39 as that of the fluoride. These values are also in good agreement with those already reported (29.8 °C and hydration number 38.3).[9] The chloride solution was stable even at very high concentrations. The solid phase which appears from the solution greater than $X=0.088$ (eutectic composition at 26.9 °C) seems to be anhydrous.

The phase diagram of the bromide system also indicates the formation of a clathrate hydrate. The clathrate hydrate formation of $(i\text{-}C_5H_{11})_4NBr$ has not been reported so far. However, the congruent melting point and the composition of it could not be determined because of the occurrence of liquid-liquid phase separation at 30.1 °C. The amount of water in the solid separated from a solution (X=0.005) which had been kept at 10 °C was determined by the Karl Fischer titration method. The mean hydration number was 54.1 for the initial wet sample, and was 36.4 and 0.4 for the solid which had been kept at about 10 °C and allowed to stand in contact with air for 3 h and 48 h, respectively. These results indicate that the solid which is in equilibrium with an aqueous solution at low temperatures has a large amount of water, characteristic of a clathrate hydrate, and the solid kept standing in air gradually loses its water with time owing to an efflorescence. This is a characteristic often found for the clathrate hydrates of quaternary ammonium salts.[2)]

The solid phase which appears in the concentration region of X=0.17—0.34 seems to be either a mono hydrate or an anhydrous salt which has a different crystal structure from that of the solid which is stable at temperatures higher than 44.5 °C.

The similarity of the log X *vs.* T^{-1} curve at low temperatures for the iodide system to those of the other systems indicates that iodide also can form a clathrate-like hydrate in the temperature range between an eutectic point (near 0 °C) and an incongruent melting point (13.3 °C). Analogous water analyses for the solid phase separated from its solution phase at 10 °C showed that the mean hydration number was 75.6 for the wet solid sample just after filtration, and 38.9 and 0.18 for the sample which had been kept standing in contact with air for 2 d and 5 d, respectively. These results, just as in the case of the above bromide systems, also suggest that the solid phase which separates out from its solution phase at temperatures lower than 13.3 °C is a clathrate-like hydrate.

The solubility of anhydrous iodide in water is about 4—5 times larger than that of tetrapentylammonium iodide (Fig. 3) at an identical temperature.

Tetrahexylammonium Halide–Water Systems. Phase diagrams for the tetrahexylammonium halide–water systems are shown in Fig. 5. No line indicating the formation of clathrate hydrate is present in this figure. It should be noted that not only in the bromide system but also in the chloride system liquid-liquid phase separation occurs over a wide temperature range. The two liquid phases existed up to at least 100 °C.

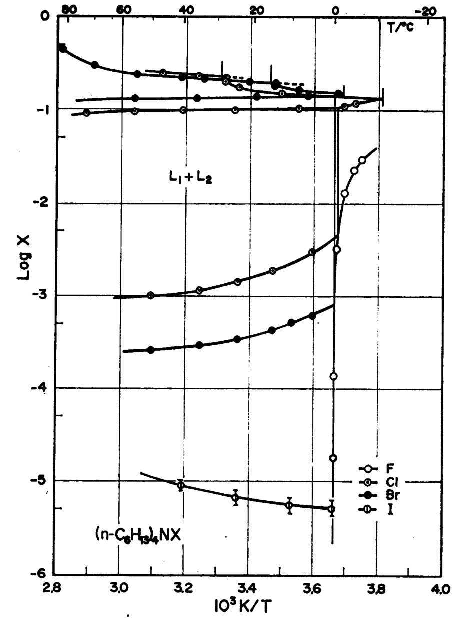

Fig. 5. Solid-liquid and liquid-liquid phase diagrams for the tetrahexylammonium halide–water systems.

In the fluoride system only the ice appeared from the solution of $X<0.03$. From the solutions greater than X=0.03 no solid phase could be formed when cooled at −30 °C for 10 d.

The chloride system shows an eutectic point (at −10.5 °C) between ice and a hydrate, with a hydration number less than 3 and an incongruent melting point at 29.6 °C. The bromide system also has similar points at −1.6 °C and 15.7 °C. The solubility of the iodide was so low that the values obtained would have errors of the order of 10—15 per cent.

Discussion

The Formation of Clathrate Hydrates. Although the formation of clathrate hydrates of $(n\text{-}C_4H_9)_4NX$ (X=F, Cl, and Br)[2,4,8,9,13)] and of $(i\text{-}C_5H_{11})_4NX$ (X=F and Cl)[9,12)] has already been known, it was newly found in this experiment that other four salts, $(n\text{-}C_5H_{11})_4NF$, $(n\text{-}C_5H_{11})_4NCl$, $(i\text{-}C_5H_{11})_4NBr$, and $(i\text{-}C_5H_{11})_4NI$, could also form a similar type of hydrates.

The two tetrapentylammonium salt hydrates have relatively low melting points (3.6 °C and −2.3 °C), as mentioned earlier. The unstableness of these hydrates may be due to the fact that a pentyl group is somewhat too long[2)] to be accomodated stably within a hydrogen-bonded water cage such as a tetrakai- or pentakaidecahedron. Judging from the hydration number of 39, the crystal structure of these hydrates is presumed to resemble that of a tetraisopentylammonium fluoride hydrate[12)] (hydration number 39) rather than that of tetrabutylammonium fluoride hydrate[13)] (hydration number 30).

Although an accurate hydration number of the $(i\text{-}C_5H_{11})_4NBr$ and of the $(i\text{-}C_5H_{11})_4NI$ hydrates cannot be determined owing to the absence of congruent melting points, it may be assumed to be around 39 taking into consideration: (1) the similarity of log X *vs.* T^{-1} curves at temperatures lower than each incongruent melting point to those of the other fluoride and bromide systems and (2) the above mentioned results of water analyses for the solid separated from its aqueous solution. However, for the bromide hydrate, there is a possibility that some hydrates which have a slightly different hydration number are formed, as in the case of $(n\text{-}C_4H_9)_4NBr$ hydrate, since its log X *vs.* T^{-1} curve becomes almost vertical to the T^{-1} axis at temperatures 29.7—29.9 °C.

The formation of a clathrate hydrate of any other quaternary ammonium iodides has not been reported so far. The fact that $(i\text{-}C_5H_{11})_4NI$ can actually form such a hydrate manifests that the lattice distortion arising from the presence of a large iodide anion can be overcome by the ability of the isopentyl group to stabilize the surrounding hydrogen-bonded water frameworks.[2)]

Furthermore, it should be noted that, at temperatures higher than the incongruent point (13.3 °C), the iodide hydrate decomposes into an anhydrous solid and a dilute aqueous solution (around 0.3 wt%). This property would be appropriate to an application of the salt such as the purification of saline water through a cyclic process of the formation and the decomposition of the hydrate.

Solubilities of Tetraalkylammonium Halides in Water. These results clearly show the solubilities of symmetrical tetraalkylammonium halides in water at a definite temperature are affected not only by the type of alkyl chain of the cation and the type of the gegen ion but also by such phenomena as the formation of a clathrate-like hydrate and the separation into two liquid phases. The solubilities of R_4NX in water at 25 °C, which are obtained from the diagrams, are summarized in Table 2, together with the values taken from some recent references.

TABLE 2. SOLUBILITIES OF SYMMETRICAL TETRAALKYLAMMONIUM HALIDES (R_4NX) IN WATER AT 25 °C (IN MOLALITY)

R	X			
	F	Cl	Br	I
CH_3	—	*ca.* 19.1[1]	6.3±0.2[14]	0.2715[15]
C_2H_5	—	*ca.* 9.5[1]	15.0±0.2[14]	1.75[16]
n-C_3H_7	Extremely high	19.00	10.73 (10.4±0.2[14])	0.6255
n-C_4H_9	12.52 (0.93)[a]	20.53	21.48	0.0679 (0.0622[6])[b]
n-C_5H_{11}	—	40.20	0.2318	0.0018 (0.0025[6])[b]
n-C_6H_{13}	—	0.088[c]	0.019[c]	0.0004

a) Solid phase is a clathrate hydrate. b) At 26 °C. c) Values for water-rich phase in two-liquid phase systems.

For a series of salts having the same alkyl chain, the solubilities decrease with changing X in the order Cl, Br, and I, with the exception of $(C_2H_5)_4NBr$ and $(n\text{-}C_4H_9)_4NBr$. However, the solubilities of a group of salts having the same anion do not show a monotonous change with increasing its alkyl-chain length. Eventually, the alkyl chain which gives the maximum solubility is reduced to n-C_5H_{11} for the chloride, n-C_4H_9 for the bromide, and C_2H_5 for the iodide.

The approximate values of the solubility ratios for salts with different anions are shown in Table 3. It is interesting to note that, among these figures, relatively high values are seen for tetrabutylammonium salts (except for m_{Cl}/m_{Br}) and tetrapentylammonium salts. The ratio m_{Cl}/m_I for the $(n\text{-}C_5H_{11})_4NX$ salts is exceptionally high, as a result of very high solubility of the chloride and very low solubility of the iodide (Table 2). These high values will give a suitable condition for the separation of one halide anion from another through, for example, the distribution equilibrium between an aqueous phase and an organic phase. It was observed that, when a 0.08 m NaI aqueous solution was equilibrated at 25 °C with an equal volume of chloroform after addition of $(n\text{-}C_4H_9)_4NCl$ in amounts equimolar with NaI, 90.4 percent of the I^- ion which had been originally present in the aqueous phase was transferred into the chloroform phase in the form of $(n\text{-}C_4H_9)_4NI$ which is sparingly soluble in water (Table 2) and very soluble in chloroform (67.8 wt% at 25 °C). A more extensive study of the distribution equilibrium is under way and will appear in near future.

TABLE 3. THE SOLUBILITY RATIOS (IN WATER AT 25 °C) FOR SYMMETRICAL TETRAALKYLAMMONIUM HALIDES (R_4NX) HAVING DIFFERENT ANIONS

R	m_{Cl}/m_{Br}	m_{Cl}/m_I	m_{Br}/m_I
CH_3	3.0	70	23
C_2H_5	0.6	5	8
n-C_3H_7	1.8	30	17
n-C_4H_9	1.0	302	316
n-C_5H_{11}	173	22800	132

Appendix

Phase Diagrams of Bolaform Salt $[(n\text{-}C_4H_9)_3N(CH_2)_6N(n\text{-}C_4H_9)_3]X_2$*–Water Systems.* The formation of clathrate hydrates of this series of salts (except for iodide) has already been reported.[4] The entire phase diagrams of the binary mixture of this type of salts with water have also been determined in this study and are shown in Fig. 6. These diagrams are similar to those of the $(n\text{-}C_4H_9)_4NX$–water systems (Fig. 2).

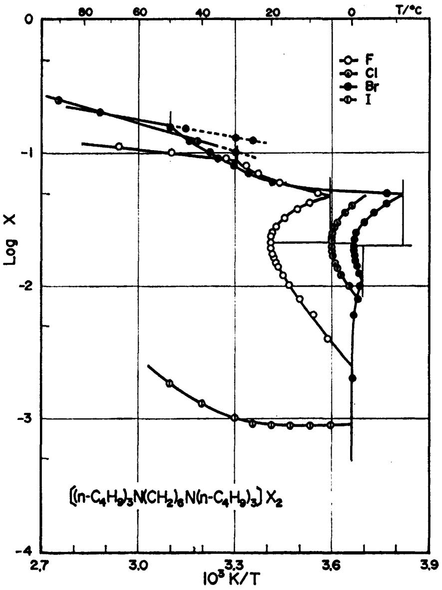

Fig. 6. Solid-liquid phase diagrams for the $[(n\text{-}C_4H_9)_3N(CH_2)_6N(n\text{-}C_4H_9)_3X_2$–water systems.

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