The Formation of Clathrate-like Hydrates of Tetrabutylammonium Halogenated Carboxylates*

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Abstract. The solid–liquid phase diagrams of binary mixtures of tetrabutylammonium halogenated carboxylates with water were examined in order to confirm the formation of clathrate-like hydrates. It was found that, among thirteen carboxylates examined, four carboxylates having CH_2FCOO^-, CHF_2COO^-, CF_3COO^-, and CH_2ClCOO^-, formed a hydrate with hydration numbers around 30 and seven carboxylates having $CHCl_2COO^-$, CCl_3COO^-, CH_2BrCOO^-, $CHBr_2COO^-$, CBr_3COO^-, $CH_3CHClCOO^-$, and $CH_3CHBrCOO^-$ formed a hydrate with hydration numbers around 23. The latter hydrate has not been reported earlier. The melting points of these newly found hydrates were fairly high: they lie between 10 and 16°C. The effect of Cl and Br atoms attached to the carbon atom of the α-position of a carboxylate anion both on the type of hydrate formed and on its stability was greatly different from that of a CH_3 group attached to the same position of the carboxylate anion.

Key words. Clathrate hydrate, tetrabutylammonium carboxylate hydrates.

1. Introduction

Various tetrabutylammonium carboxylates are known to form clathrate-like hydrates [1–6] similar to the so-called gas hydrates [7]. These carboxylate hydrates can be classified into two types [1]: (1) the first type of hydrate is formed by tetrabutylammonium carboxylates having small carboxylate anions ranging from $HCOO^-$ to $C_3H_7COO^-$ and has hydration numbers around 30. This hydrate is fairly stable: most of the melting points are 10–18°C. (2) The second type of hydrate is formed by carboxylates having somewhat larger carboxylate anions such as $C_4H_9COO^-$ and $C_5H_{11}COO^-$, including various isomers, and has hydration numbers around 39. This hydrate is relatively unstable: most of the melting points are lower than 10°C. Judging from the values of the hydration numbers, the first type of hydrate is assumed to be isomorphic with the well-known tetrabutylammonium fluoride, $(n\text{-}C_4H_9)_4NF$ hydrate [8] and the second one with a tetrabutylammonium benzoate, $(n\text{-}C_4H_9)_4NOOCC_6H_5$ hydrate [9].

   Although which one of the two types of hydrates is formed is mainly dependent upon the size of the carboxylate anion, the stability, i.e., the melting point, of the hydrate is dependent not only on the size of the carboxylate anion but also on its shape, especially on the presence of a substituent group in the α-position of the

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carboxylate anion [1]. The purpose of this study is to see (1) the effects of halogen atoms (F, Cl, and Br) attached to the α-position of either acetate or propionate anion both on the hydration numbers and on the melting point of the hydrate formed and (2) the difference in these effects between a halogen atom and a methyl group attached to the same position.

2. Experimental

2.1. MATERIALS

The following tetrabutylammonium carboxylates, $(n\text{-}C_4H_9)_4NOOCR$, were used, where R = CH_2F, CHF_2, CF_3, CH_2Cl, $CHCl_2$, CCl_3, CH_2Br, $CHBr_2$, CBr_3, CH_2I, CH_3CHCl, CH_3CCl_2, and CH_3CHBr. Aqueous solutions of these carboxylates were prepared by neutralizing a tetrabutylammonium hydroxide solution with the corresponding acids. The hydroxide was prepared by reacting tetrabutylammonium iodide with freshly prepared silver hydroxide in water. Tetrabutylammonium iodide was obtained by adding sodium iodide to an aqueous solution of commercially available tetrabutylammonium bromide, and was purified by repeated recrystallization from ethyl acetate. All acids were reagent grade commercial materials and used without further purification.

2.2. PROCEDURES

The solid–liquid phase diagrams of the binary $(n\text{-}C_4H_9)_4NOOCR$–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 carboxylate, and was sealed in a small glass ampule. The concentration of the mother solution was determined by a titration method using a sodium tetraphenylborate solution: a mixture containing a known amount of the mother solution (about 1×10^{-4} mol), 0.5 mL of 0.05 wt% Bromophenyl Blue solution (indicator), 10 mL of chloroform, and 10 mL of 0.1 mol dm^{-3} sodium hydroxide, was stirred vigorously with a magnetic stirrer for about 15 minutes in order to move a tetrabutylammonium ion–Bromophenyl Blue complex from an aqueous layer to the chloroform layer; the mixture was then titrated with a 0.2 mol dm^{-3} sodium tetraphenylborate solution which had been standardized with a known amount of pure tetrabutylammonium iodide, until the colour in the lower chloroform phase changed from blue to colorless.

Each ampule was gradually cooled until the solid phase appeared and was annealed for at least 24 hours at a temperature several degrees lower than the temperature at which the solid phase completely dissolved. After that, the ampule 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 disappeared was accurately determined.

It was found that two carboxylates having CH_2ICOO^- and $CH_3CCl_2COO^-$ anions could not form any hydrates. The phase diagrams of these systems were determined by measuring a solubility in water at several temperatures. In a measuring cell (3 cm diameter and 10 cm high) immersed in a constant temperature

bath, each solid was saturated in 10–20 mL of water by vigorous stirring with a magnetic stirer from 2–5 days. A known amount of saturated solution was then withdrawn and analyzed by the same titration method as described above.

The conventional partial molal volumes of carboxylate anions at 25°C were determined from the partial molal volumes of sodium carboxylates at infinite dilution using the relation that the conventional partial molal volume of Na^+ ion is equal to -1.21 mL mol^{-1} at 25°C [10]. The partial molal volumes of sodium carboxylates were determined by density measurements. Density measurements were carried out below 0.3 mol kg^{-1} with three 5 mL pycnometers and experimental results were analyzed by a conventional method [11].

3. Results and Discussion

The solid–liquid phase diagrams for the binary systems, water–$(n\text{-}C_4H_9)_4NOOCR$, where R $= CH_2F$, CHF_2, CF_3, CH_2Cl, $CHCl_2$, CCl_3, CH_2Br, $CHBr_2$, CBr_3, and CH_2I are shown in Figures 1, 2, and 3. The logarithm of the concentration expressed as a 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 each figure.

In Figure 1, all the systems of R $= CH_2F$, CHF_2, and CF_3 exhibit congruent melting points at the concentrations near $X = 0.032$, indicating that these salts can form a hydrate with hydration numbers around 30. For the system of R $= CF_3$, another solid phase appears at concentrations higher than $X = 0.042$, though the composition of this phase is not clear. The melting points of the three hydrates decrease with the increasing number of F atoms in R.

In Figure 2, the phase diagram of the salt of R $= CH_2Cl$ shows similar behavior to that of the three systems shown in Figure 1. However, two other systems of R $= CHCl_2$ and R $= CCl_3$ exhibit incongruent melting points (10.6°C and 14.6°C, respectively) at the concentrations near $X = 0.03$ and show congruent melting points near $X = 0.042$, indicating the formation of hydrates with hydration numbers around 23. The melting points of the hydrates decrease in an irregular order R $= CCl_3$, CH_2Cl, and $CHCl_2$, in contrast to the case of the fluorinated acetate hydrates shown in Figure 1.

Phase diagrams of the systems containing brominated acetates, shown in Figure 3, exhibit further complicated behavior. These behavior patterns are summarized as follows: (1) all the systems show congruent melting points at the concentrations near $X = 0.042$, indicating the formation of hydrates with hydration numbers around 23. The melting points of the hydrates decrease in the order, R $= CBr_3$, CH_2Br, and $CHBr_2$, which is identical with the case of the chlorinated acetates shown in Figure 2; (2) all the systems also exhibit incongruent melting points (8.9°C for R $= CH_2Br$, 9.7°C for R $= CHBr_2$, and 13.8°C for R $= CBr_3$). The concentration corresponding to the incongruent melting point is near $X = 0.015$ for the R $= CH_2Br$ salt, although those for the other two salts, R $= CHBr_2$ and R $= CBr_3$, are near $X = 0.03$ as in the R $= CHCl_2$ salt; (3) the slope of $\partial \log X/\partial(1/T)$ in the concentration range between $X = 0.002$ and $X = 0.015$ for the R $= CH_2Br$ system is steeper than those of the other two systems and is nearly equal to the slope found for an $(i\text{-}C_5H_{11})_4NF$ hydrate [12]. This suggests that the $(n\text{-}C_4H_9)_4NOOCCH_2Br$

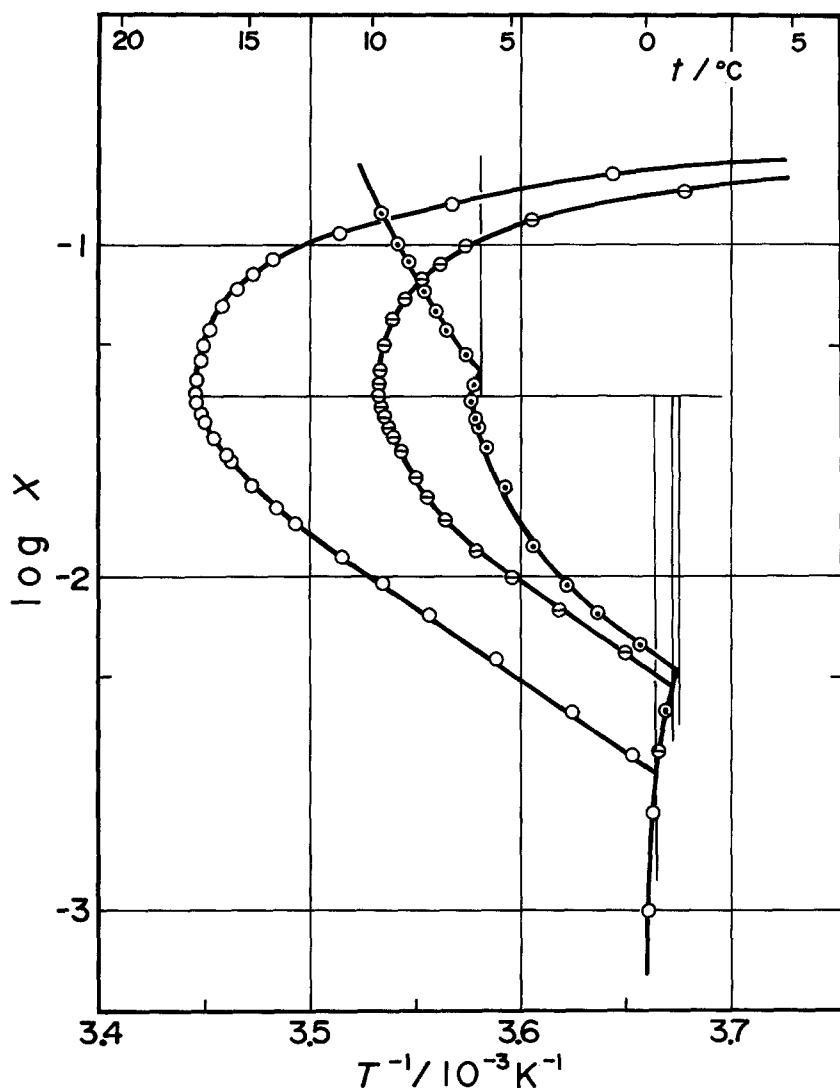Fig. 1. Solid–liquid phase diagrams for the water–$(n\text{-}C_4H_9)_4NOOCR$ systems. $\bigcirc$: $R = CH_2F$; $\ominus$: $R = CHF_2$; $\odot$: $R = CF_3$.

hydrate formed in this concentration range has hydration numbers about 40; and (4) only the salt of $R = CHBr_2$ exhibits another congruent melting point near $X = 0.080$, i.e., a hydrate with hydration numbers 11–12. The formation of such a hydrate has never been known for a series of tetrabutylammonium salt hydrates. Figure 3 also includes the phase diagram of the salt of $R = CH_2I$. This diagram clearly shows that this salt cannot form a hydrate similar to that mentioned above.

All the melting points and the hydration numbers, determined from each congruent melting point and congruent composition, are summarized in Table I, together with those of two propionates of $R = CH_3CHCl$ and CH_3CHBr. For

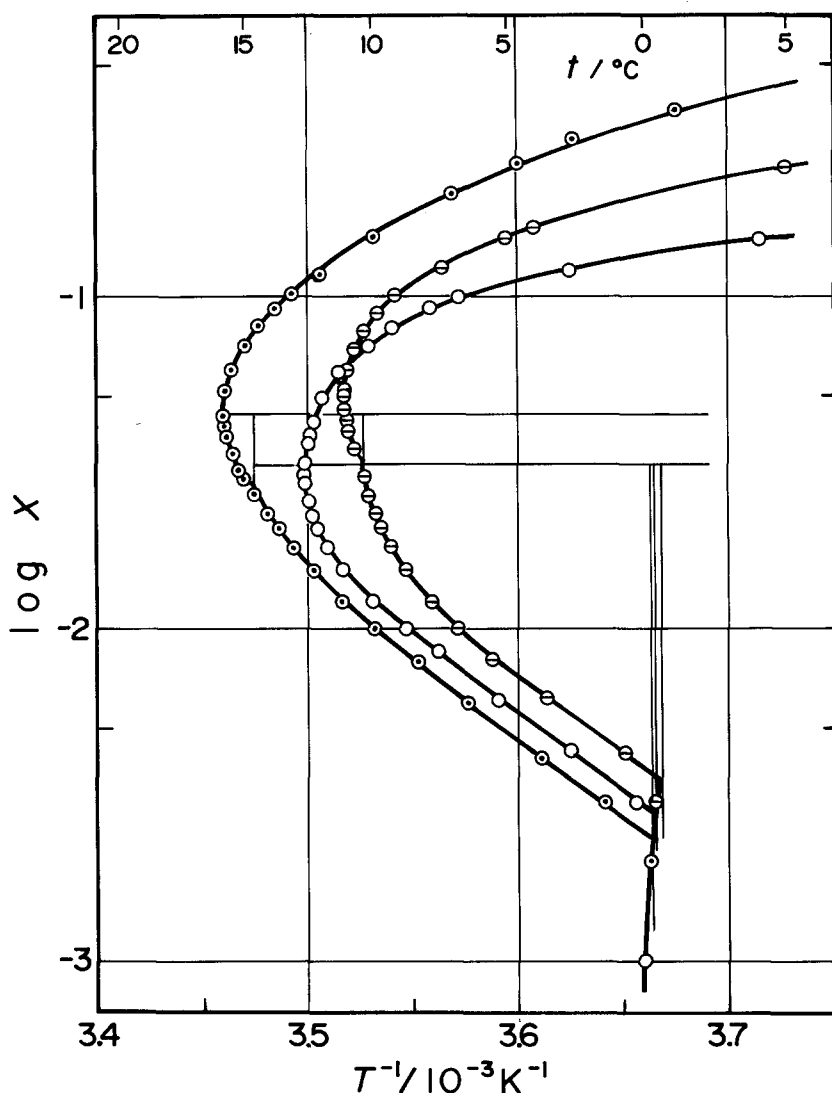Fig. 2. Solid–liquid phase diagrams for the water–$(n\text{-}C_4H_9)_4NOOCR$ systems. $\bigcirc$: $R = CH_2Cl$; $\ominus$: $R = CHCl_2$; $\odot$: $R = CCl_3$.

comparison, Table I also includes the results previously reported [1] for similar kinds of carboxylates with R having no halogen atoms. The most remarkable features of these results are summarized as follows: (1) except for the $R = CHBr_2$ hydrate with hydration numbers around 11, all the hydrates can be classified into two types of hydrates, i.e., the one with hydration numbers around 30 and the other around 23; (2) although the hydrates with hydration numbers around 30 may be considered to be the same type of hydrate as a $(n\text{-}C_4H_9)_4NF$ hydrate [8], the hydrates with · hydration numbers around 23 have not been reported earlier; (3) these newly
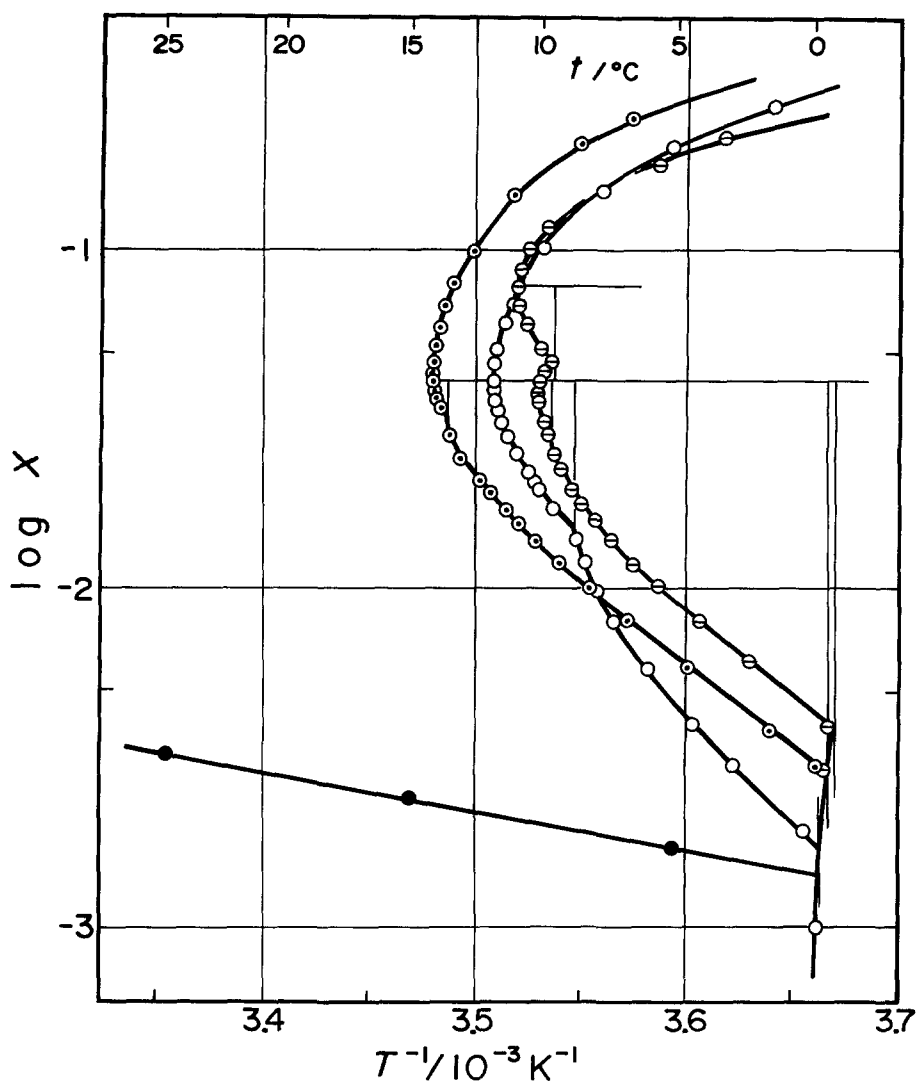
Fig. 3. Solid–liquid phase diagrams for the water–$(n\text{-}C_4H_9)_4NOOCR$ systems. $\bigcirc$: $R = CH_2Br$; $\ominus$: $R = CHBr_2$; $\odot$: $R = CBr_3$; $\bullet$: $R = CH_2I$.

discovered hydrates are formed only by halogenated carboxylates; and (4) the hydrates with hydration numbers around 39, which are mentioned in the introduction, cannot be formed by any carboxylates investigated. Only for the carboxylate with $R = CH_2Br$, the formation of this type of hydrate is expected in a dilute concentration range between $X = 0.002$ and $X = 0.015$, as pointed above.

In order to consider the effect of carboxylate anions both on the type and the melting point of the hydrate formed, the melting point of each hydrate is plotted against the conventional partial molal anionic volume $\bar{V}^0_{conv}$ at 25°C in Figure 4. The $\bar{V}^0_{conv}$ is used as an indication of the effective volume of an anion within the

Table I. Melting points and hydration numbers of the clathrate-like hydrates formed by a series of tetrabutylammonium carboxylates, $(n\text{-}C_4H_9)_4NOOCCR_1R_2R_3$

Carboxylate	R_1	R_2	R_3	Melting point (°C)	Hydration numbers
Acetate[a]	H	H	H	14.8	30 ± 1
Monofluoroacetate	H	H	F	17.1	29 ± 2
Difluoroacetate	H	F	F	10.0	29 ± 2
Trifluoroacetate	F	F	F	6.4	29 ± 1
Monochloroacetate	H	H	Cl	12.7	31 ± 2
Dichloroacetate	H	Cl	Cl	11.1	22 ± 2
Trichloroacetate	Cl	Cl	Cl	15.8	23 ± 2
Monobromoacetate	H	H	Br	12.2	23 ± 2
Dibromoacetate	H	Br	Br	10.3	24 ± 1
				11.2	11 ± 3
Tribromoacetate	Br	Br	Br	14.6	23 ± 2
Propionate[a]	H	H	CH_3	18.0	30 ± 1
Isobutyrate[a]	H	CH_3	CH_3	9.8	30 ± 1
Pivalate[a]	CH_3	CH_3	CH_3	−0.7	30 ± 2
α-Chloropropionate	H	CH_3	Cl	12.5	22 ± 2
α-Bromopropionate	H	CH_3	Br	10.8	23 ± 2

[a] Reference [1].

hydrate solid. Open circles represent the hydrate with hydration numbers around 30 and filled circles represent the one around 23. From the density measurements the following thirteen conventional partial molal anionic volumes are newly obtained in this study: 44.7, 49.1, 59.9, 50.8, 65.0, 82.9, 55.8, 80.1, 108.8, 66.5, 69.7, 70.2, and 84.9 $cm^3\,mol^{-1}$ for CH_2FCOO^-, CHF_2COO^-, CF_3COO^-, CH_2ClCOO^-, $CHCl_2COO^-$, CCl_3COO^-, CH_2BrCOO^-, $CHBr_2COO^-$, CBr_3COO^-, $CH_3CHClCOO^-$, $CH_3CHBrCOO^-$, $(CH_3)_2CHCOO^-$, and $(CH_3)_3CCOO^-$, respectively. Other $\bar{V}^0_{conv}$ values are taken from the literature [10]. For comparison, Figure 4 also includes similar relationships for a series of hydrates of tetrabutylammonium inorganic salts (line A) [13] and of simple tetrabutylammonium carboxylates with corboxylate anions from $HCOO^-$ to $n\text{-}C_3H_7COO^-$ (line B) [1]. All the hydrates with hydration numbers around 30 may be assumed to be isomorphic with a $(n\text{-}C_4H_9)_4NF$ hydrate [8], as pointed out in the introduction. The line A, which indicates that the melting point of the hydrate decreases almost linearly with increasing the molal volume of the anion including $HCOO^-$, can be explained by the distortion effect caused by the anion on the hydrogen-bonded water framework in the hydrate [13]. The behavior of the line B differs greatly from the line A. This has been explained by considering an enclathration of alkyl groups of such carboxylate anions as CH_3COO^-, $C_2H_5COO^-$, and $C_3H_7COO^-$ within a vacant pentagonal dodecahedron which exists in a gap between other polyhedra enclosing each butyl group of the tetrabutylammonium cation [1]. The highest melting point of the propionate hydrate would result from the best fit of the propionate anion within the pentagonal dodecahedron.
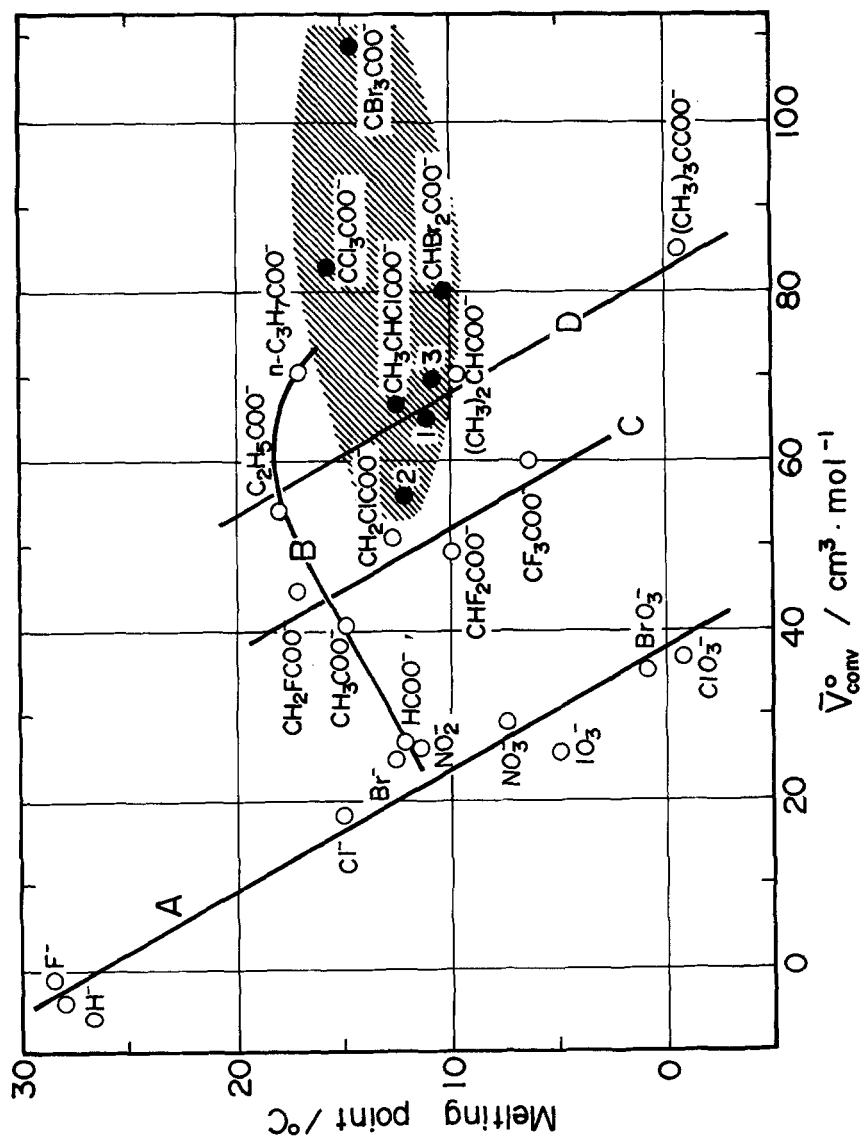
Fig. 4. Relationship between the melting points of the hydrates of tetrabutylammonium salts, $(n\text{-}C_4H_9)_4NX$, and the conventional partial molal anionic volumes of the anion X. Anion is shown by the side of each point and the numbers 1, 2, and 3 indicate $CHCl_2COO^-$, CH_2BrCOO^-, and $CH_3CHBrCOO^-$, respectively. Open circle is a hydrate with hydration numbers around 30 and filled one around 23. The explanation of the lines A–D is given in the text.

It is interesting to note that, for other carboxylate hydrates with hydration numbers around 30, two further lines (lines C and D) can be drawn as lines almost parallel to line A. These lines may be explained by the same distortion effect of anions as the line A, i.e., the distortion of the water network caused by the successive replacement of a H atom of the CH_3COO^- anion by a F (or Cl) atom for the line C, and similarly by the replacement of a H atom in the α-position of the $CH_3CH_2COO^-$ anion by a CH_3 group for the line D. A slightly higher melting point of the monofluoroacetate hydrate than that of the acetate hydrate would indicate a better fit of the CH_2FCOO^- anion in a pentagonal dodecahedron than the CH_3COO^- anion. In conclusion, the stabilities, i.e. the melting points, of the tetrabutylammonium salt hydrates with hydration numbers around 30 can be correlated with the partial molal volumes of the anion.

However, for the newly found hydrates with hydration numbers around 23, any simple explanation cannot be given for the relationship between the melting point and the partial molal volume of the anion. The region in which these hydrates are formed is represented by the hatched area in Figure 4. It is noteworthy that the hatched region is limited to large anionic volumes ($\bar{V}^0_{conv} > 55 \text{ cm}^3 \text{ mol}^{-1}$) and to fairly high melting points (between 10 and 16°C). Although the following three anions, $(CH_3)_2CHCOO^-$, $CH_3CHClCOO^-$, and $CH_3CHBrCOO^-$, have similar values of $\bar{V}^0_{conv}$, only the salt having the $(CH_3)_2CHCOO^-$ anion, tetrabutylammonium isobutyrate, forms a hydrate with hydration numbers around 30 and the salts having the other two anions form hydrates of around 23. More markedly, tetrabutylammonium pivalate, $(n\text{-}C_4H_9)_4NOOCC(CH_3)_3$, forms a very unstable hydrate (mp = -0.7°C) with a hydration number around 30, whereas the salt having either CCl_3COO^- or $CHBr_2COO^-$ forms quite a stable hydrate with a hydration number around 23, in spite of almost similar values of $\bar{V}^0_{conv}$ for these three anions. These facts clearly indicate that the effects of the Cl and Br atoms attached to the α-position of a carboxylate anion both on the structure and on the stability of a hydrate are very different from that of a CH_3 group attached in the same position. The reason for this difference is not clear at present. However, the following fact will, at least partly, contribute to this difference: a spherical Cl or Br atom is uniformly voluminous in all directions with respect to a C—Cl or C—Br bond, whereas the CH_3 group protrudes towards three directions owing to three C—H bonds if free rotation with respect to the C—CH_3 bond is restricted by the hydrogen-bonded water network in the vicinity of the CH_3 group. Although there is no information about the structure of this new type of hydrate, the existence of fairly large polyhedra enclosing such bulky carboxylate anions as CCl_3COO^- and CBr_3COO^- may be expected from the fact that the hydration numbers are quite small (around 23) as compared with those of the typical type of hydrates (around 30 or 39).

Among the tetrabutylammonium carboxylates examined in this study, two carboxylates with CH_2ICOO^- and $CH_3CCl_2COO^-$ anions could not form hydrates similar to those mentioned above. The solubilities of these salts in water were found to be 0.097, 0.133, and 0.183 mol kg^{-1} for $(n\text{-}C_4H_9)_4NOOCCH_2I$ and 0.103, 0.102, and 0.104 mol kg^{-1} for $(n\text{-}C_4H_9)_4NOOCCCl_2CH_3$ at 5, 15, and 25°C, respectively. The solid phase which is in equilibrium with a saturated aqueous phase seems to be anhydrous for both salts.

Acknowledgement

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