Hydrates of Organic Compounds. XIV. The Formation of Clathrate-Like Hydrates of Tetrabutylammonium Amino Carboxylates

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(Received March 24, 1987)

Synopsis. The solid-liquid phase diagrams of binary mixtures of water with a series of tetrabutylammonium α-amino carboxylates, $(n\text{-}C_4H_9)_4NOOCCH(NH_2)R$ (R=H, CH_3, C_2H_5, $n\text{-}C_3H_7$, and $(CH_3)_2CH$), were examined. It was found that all the salts examined could form hydrates with hydration numbers either around 30 or around 39.

A series of tetrabutylammonium carboxylates has been known to form a clathrate-like hydrate[1] similar to the so-called gas hydrate.[2] According to a crystal structural analysis by Jeffrey et al. on a tetrabutylammonium benzoate hydrate,[3] oxygen atoms of the benzoate anion are incorporated into the water lattice, making an anionic host structure. The characteristics found for the tetrabutylammonium carboxylate hydrates are summarized as follows: (1) Two types of hydrates exist; group I which has fairly high melting points and hydration numbers around 30 and group II which has relatively low melting points and hydration numbers around 39; and (2) a methyl group attached to the carbon atom of the α-position of the carboxylate anion pronouncely lowers the stability of the hydrate due to a deformation effect imposed on the host structure.[1]

In this study, the solid-liquid phase diagrams for binary mixtures of a series of tetrabutylammonium α-amino carboxylates with water were examined in order to determine (1) whether these amino carboxylates can form similar types of clathrate-like hydrates and (2) the degree of distortion effect of a NH_2 group attached to the carbon atom of α-position on the stability of the hydrate.

Experimental

An aqueous solution of tetrabutylammonium amino carboxylates was prepared by the neutralization of a tetrabutylammonium hydroxide solution with each amino acid. The hydroxide solution was prepared by the same procedure as described in previous papers.[1,4] All amino acids were purchased from Tokyo Kasei Kogyo Co. Ltd., and were purified by a conventional method: A hot aqueous solution of an amino acid was added dropwise to 95 v/v% ethyl alcohol with stirring, followed by filtration of a solid phase and by washing the solid with 95 v/v% ethyl alcohol.

Solid-liquid phase diagrams for the binary systems of water-tetrabutylammonium amino carboxylates were determined in the same manner as described in the previous papers[1,4] (an ampoule method).

Results and Discussion

The solid-liquid phase diagrams for binary systems of tetrabutylammonium aminoacetate (glycine salt)-water and of tetrabutylammonium DL-α-aminopropionate (alanine salt)-water are shown in Fig. 1. Similar phase diagrams for binary systems of tetrabutylammonium DL-α-aminoisobutyrate (valine salt)-water and of tetrabutylammonium DL-α-aminopentanoate (norvaline salt)-water are shown in Fig. 2. In these figures the logarithm of the concentration expressed in the mole fraction, X, is plotted against the reciprocal of the absolute temperature. The temperature, expressed in ordinary Celcius units, is shown on the upper side of the figure. Because of the similarity of the phase diagram of tetrabutylammonium DL-α-aminobutyrate-water system with that of the tetrabutylammonium DL-α-aminopropionate-water system, the phase diagram of the former system is excluded from Fig. 1.

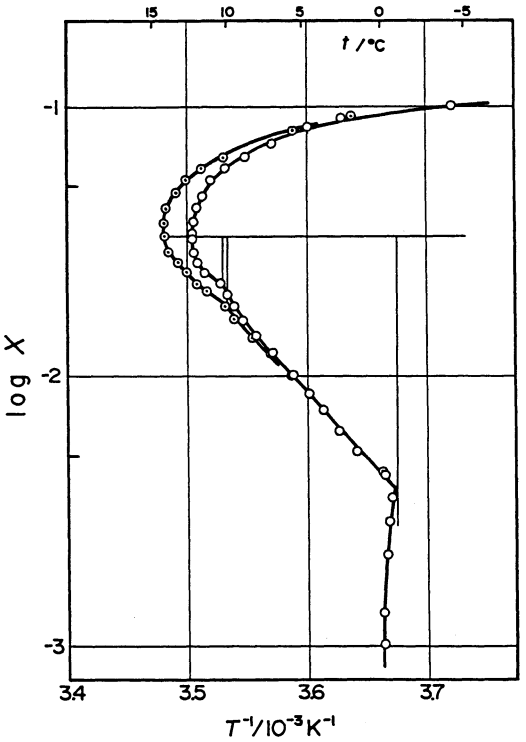

Fig. 1. Solid-liquid phase diagrams for the tetrabutylammonium aminoacetate-water system (◉) and for the tetrabutylammonium DL-α-aminopropionate-water system (○).

The existence of congruent melting points at $X\simeq0.032$ in Fig. 1 and at $X\simeq0.025$ in Fig. 2 clearly indicates that these salts form a hydrate which has large hydration numbers: the congruent composition of $X\simeq0.032$ corresponds to a hydrate whose hydration numbers are around 30 and of $X\simeq0.025$ to the one with hydration numbers around 39. Judging from such large hydration numbers, these hydrates seem to be

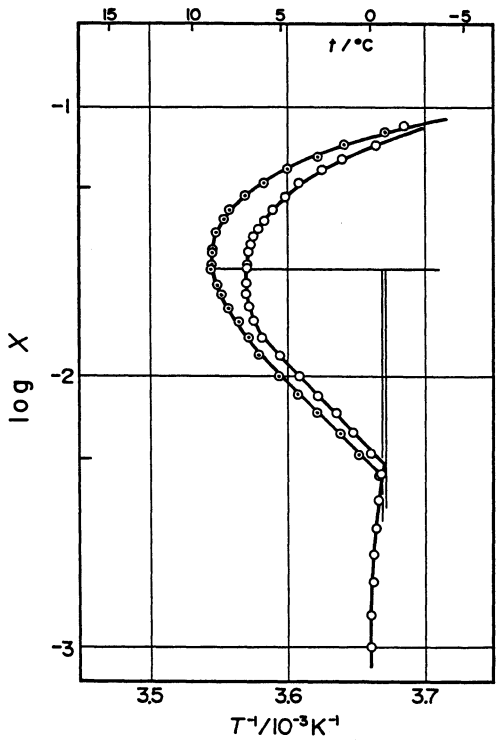

Fig. 2. Solid-liquid phase diagrams for the tetrabutylammonium DL-α-aminoisobutyrate–water system (○) and for the tetrabutylammonium DL-α-aminopentanoate–water system (◉).

clathrate-like hydrates, similar to $(n\text{-}C_4H_9)_4NF\cdot 30H_2O$[5] and $(n\text{-}C_4H_9)_4NOOCC_6H_5\cdot 39.5H_2O$[3] hydrates. The presence of tetrabutylammonium amino carboxylate hydrates has never been known before. As can be seen in Fig. 1, phase diagrams of the tetrabutylammonium aminoacetate–water system and the tetrabutylammonium DL-α-aminopropionate–water system show an incongruent melting point of 10.1 °C at $X\simeq 0.018$ and of 10.4 °C at $X\simeq 0.022$, respectively. The exact hydration numbers of the hydrates formed in the concentration range between eutectic composition ($X\simeq 0.004$) and the concentration corresponding to the incongruent point are not obvious at present.

All the melting points and hydration numbers, determined from each congruent melting point and congruent composition are summarized in Table 1. From these results the clathrate-like hydrates of tetrabutylammonium DL-α-amino carboxylates can be classified into two groups, group I and group II, just as in the case of tetrabutylammonium carboxylate hydrates.[1] The classification of group I and II is also given in Table 1. The group I hydrate, whose hydration numbers are around 30, has fairly high melting points and is formed by amino carboxylates with small alkyl groups. The group II hydrate, whose hydration numbers are around 39, has relatively low melting points and is formed by amino carboxylates with relatively large alkyl groups.

In previous studies[1,4,6] it became clear that the melting point of tetrabutylammonium salt hydrate is largely dependent upon the molar volume of the anion

Table 1. Melting Points and Hydration Numbers of Clathrate-Like Hydrates of Tetrabutylammonium DL-α-Amino Carboxylates $(n\text{-}C_4H_9)_4NOOCCH(NH_2)R$

R	Mp θ_m/°C	Hydration number	Group
H	14.2	30±1	I
CH_3	12.3	30±2	I
CH_3CH_2	12.2	30±2	I
$(CH_3)_2CH$	6.9	39±2	II
$CH_3(CH_2)_2$	8.9	38±2	II

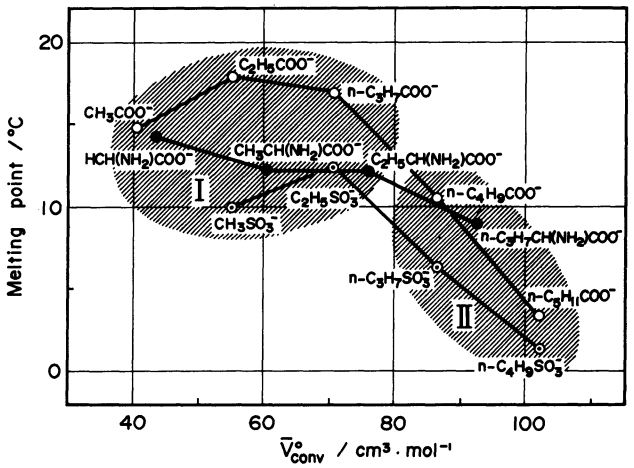

Fig. 3. Relationship between the melting points of the tetrabutylammonium DL-α-amino carboxylate hydrates and the conventional partial molar volumes of DL-α-amino carboxylate anions. The same relationships for tetrabutylammonium carboxylate hydrates[1] and tetrabutylammonium alkanesulfonate hydrates[4] are also shown.

of the salt. This relation is represented in Fig. 3, in which the melting point of each hydrate is plotted against the conventional partial molar anionic volume at 25 °C as an indication of the effective volume of the anion within the hydrate solid.[6] The conventional partial molar volume of each amino carboxylate anion was obtained from the literature.[7] In Fig. 3 the same relationships for a series of tetrabutylammonium carboxylate hydrates[1] and of tetrabutylammonium alkanesulfonate hydrates[4] are also shown. Although the dependence of the melting point of the amino carboxylate hydrates upon the anionic volume is not so marked as compared with the other two series of hydrates, the region in which either the group I hydrate or the group II hydrate is formed is essentially identical for the three types of hydrates. For this reason, concerning the crystal structure of the amino carboxylate hydrates, the same speculation as was done regarding both the carboxylate hydrates and the alkanesulfonate hydrates may be made: The group I hydrate is iso-structural with $(n\text{-}C_4H_9)_4NF$ hydrate[5] and a vacant pentagonal dodecahedron is occupied by a small alkyl group, such as CH_3 and C_2H_5, of the amino carboxylate anion; and the group II hydrate is iso-structural with $(n\text{-}C_4H_9)_4NOOCC_6H_5$ hydrate[3] and the amino carboxylate anion like $CH_3(CH_2)_2CH(NH_2)$-

Table 2. Melting Points of Clathrate-Like Hydrates of Three Types of Tetrabutylammonium Carboxylates

R	Mp θ_m/°C Carboxylate anion		
	RCH_2COO^- a)	$RCH(NH_2)COO^-$ b)	$RCH(CH_3)COO^-$ a)
H	14.8(I) c)	14.2(I)	18.0(I)
CH_3	18.0(I)	12.3(I)	9.8(I)
CH_3CH_2	17.0(I)	12.2(I)	7.7(II)
$(CH_3)_2CH_2$	11.3(II)	6.9(II)	—
$CH_3(CH_2)_2$	10.6(II)	8.9(II)	5.1(II)

a) Taken from the Ref. 1. b) DL except for the R=H salt. c) I and II in parentheses indicate the group of the hydrates.

COO^- and $(CH_3)_2CHCH(NH_2)COO^-$ is enclathrated within a large polyhedron, such as tetrakaidecahedron and pentakaidecahedron.

In Table 2 the melting points of the hydrates of three types of tetrabutylammonium carboxylates (ordinary carboxylates,[1] DL-α-amino carboxylates and α-methyl carboxylates[1]) are compared with each other. This table clearly indicates that the effect of a NH_2 group upon the melting points of the hydrate is generally intermediate between that of a H group and of a CH_3 group. However, it is interesting to note that (1) the melting point of the tetrabutylammonium aminoacetate hydrate (14.2 °C) is almost the same as that (14.8 °C) of the tetrabutylammonium acetate hydrate, in spite of the situation that a slightly bulky $CH_2(NH_2)$ group is expected to be more suitable for being intercalated within a pentagonal dodecahedron than a CH_3 group; and (2) the melting point of the valine salt hydrate (6.9 °C) is lower than that of the norvaline salt hydrate (8.9 °C), in contrast to the slightly higher melting point (11.3 °C) of tetrabutylammonium isovalerate hydrate as compared with that of tetrabutylammonium pentanoate hydrate (10.6 °C). These phenomena may be explained by the formation of hydrogen bonding between the NH_2 group and water lattice since the configuration of the group attached to the carbon atom of α-position is restricted if both the COO^- group and the NH_2 group make hydrogen bonding with water lattice at the same time. Though the effect of the formation of a hydrogen bonding between the NH_2 group and water lattice upon the stability of the hydrates is not so eminent, this effect will lead to the anticipation that there will be some difference in the melting points of the hydrates between a D-amino carboxylate and of a L-amino carboxylate. Preliminary experiments for α-aminopropionate and α-aminoisobutyrate hydrates showed that the melting points of the hydrates were slightly different between the D and the L isomers. Precise investigations are now in progress.

The present work was supported by a Grant-in-Aid for Scientific Research No.60470006 from the Ministry of Education, Science and Culture.

References

1) H. Nakayama and S. Torigata, *Bull. Chem. Soc. Jpn.*, **57**, 171 (1984).
2) W. F. Claussen, *J. Chem. Phys.*, **19**, 259, 662 (1951). M. von Stackelberg and H. R. Muller, *ibid.*, **19**, 1319 (1951). L. Pauling and R. E. Marsh, *Proc. Natl. Acad. Sci. U.S.A.*, **38**, 112 (1952).
3) M. Bonamico, G. A. Jeffrey, and R. K. McMullan, *J. Chem. Phys.*, **37**, 2219 (1962).
4) H. Nakayama and H. Usui, *Bull. Chem. Soc. Jpn.*, **59**, 833 (1986).
5) D. Feil and G. A. Jeffrey, *J. Chem. Phys.*, **35**, 1863 (1961).
6) H. Nakayama, *Bull. Chem. Soc. Jpn.*, **56**, 877 (1983).
7) S. Cabani, G. Conti, E. Matteoli, and M.R. Tiné, *J. Chem. Soc., Faraday Trans. 1*, **77**, 2377 (1981).