

THE EFFECT OF CARBOXYLATE ANIONS ON THE FORMATION OF CLATHRATE HYDRATES
OF TETRABUTYLAMMONIUM CARBOXYLATES

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ABSTRACT. The solid-liquid phase diagrams of binary mixtures of water with tetrabutylammonium carboxylate having an unsaturated alkyl group in the carboxylate anion $((n-C_4H_9)_4NOOCR; R=C_2H_3-C_9H_{17})$ were examined in order to confirm the formation of clathrate-like hydrates. The results are summarized as follows: (1) the formation of a clathrate-like hydrate is newly confirmed for all the 13 carboxylates examined; (2) these hydrates are classified into three groups I, II, and III on the basis of the hydration numbers; (3) the group I hydrates, which are formed by the carboxylates with $R=C_2$ and $R=C_3$, have hydration numbers around 30 and are the most stable hydrates among those examined in this study; (4) the group II hydrates, with hydration numbers around 39, are formed by all the carboxylates with $R=C_4$ and C_5 including sorbate and are less stable than the group I hydrates; (5) the group III hydrates, with hydration numbers around 30 like the group I hydrates, are formed by carboxylates with long alkyl chains such as 2-octenoate and 2-decenoate and are generally unstable.

1. INTRODUCTION

In a previous paper¹⁾ the formation of a clathrate-like hydrate by a series of tetrabutylammonium carboxylates $((n-C_4H_9)_4NOOCR)$ with a saturated alkyl group in the carboxylate anion was confirmed from the solid-liquid phase diagrams and these hydrates were classified into three groups, I, II, and III, on the basis of the hydration numbers. The main characteristics for these three groups of hydrates are summarized as follows:

(1) The group I hydrates include the hydrates formed by the carboxylates with $R=H, CH_3, C_2H_5, n-C_3H_7, i-C_3H_7,$ and $t-C_4H_9$. These hydrates are fairly stable. From the fact that the hydration number is around 30 the crystal structure of the hydrate seems to be isomorphous with that of a well-known tetrabutylammonium fluoride hydrate.²⁾ Since 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, as discussed in the previous paper,^{1,3)} it has been

concluded that such alkyl groups as CH_3 , C_2H_5 , and C_3H_7 are located in a vacant pentagonal dodecahedron. Similar consideration has also been proposed by Dyadin et al.⁴⁾ on the basis of X-ray diffraction characteristics.

(2) The group II hydrates are formed exclusively by all the carboxylates with $\text{R}=\text{C}_4\text{H}_9$ and C_5H_{11} except for $t\text{-C}_4\text{H}_9$, and have hydration numbers around 39. The crystal structure of these hydrates seems to be essentially the same as that of the tetrabutylammonium benzoate hydrate, which has an ideal composition of $(n\text{-C}_4\text{H}_9)_4\text{NOOCC}_6\text{H}_5 \cdot 39.5\text{H}_2\text{O}$ ⁵⁾, in which the benzoate anion is surrounded by one large water cage. From the relationship between the melting points of the hydrates and the shape of an alkyl group in the carboxylate anion, it has been concluded that the methyl group attached to the carbon atom of 2-position causes a considerable distortion in the hydrogen-bonded water framework.

(3) The formation of a clathrate-like hydrate for the tetrabutylammonium carboxylates with long alkyl chains ranging from $n\text{-C}_6\text{H}_{13}$ to $n\text{-C}_{10}\text{H}_{21}$ is clearly confirmed from the phase diagrams. These hydrates are classified as the group III hydrates. The hydration number is around 30, just as in the group I hydrates, and the melting points are very low. From the fact that the hydration number is around 30, the possible crystal structure of these hydrates will be that they are isomorphous with $(n\text{-C}_4\text{H}_9)_4\text{NF}$ hydrate and the long alkyl chain in the carboxylate anion penetrates into two (or three) pentagonal dodecahedra which are face-sharing with each other.

In this paper new results for a similar type of investigation about unsaturated carboxylates are presented and discussed from a similar point of view. The main objectives of this investigation are (1) new confirmation of the formation of a clathrate-like hydrate of tetrabutylammonium unsaturated carboxylates and (2) an examination of the influence of the presence of a double bond in the alkyl group of the carboxylate anion (such as the change in chain length, the decrease in chain flexibility, and the decrease in the number of hydrogen atoms) upon the stability of the hydrate in comparison with the case of the saturated carboxylates briefly summarized above.

2. MATERIALS AND METHODS

An aqueous solution of tetrabutylammonium unsaturated carboxylates was prepared by a reaction between tetrabutylammonium iodide and silver carboxylate 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. Since the solubilities of the silver carboxylates used in water are fairly low (for example, at 25°C , 1.30wt% for $\text{CH}_2\text{CHCOOAg}$, 0.29wt% for $\text{CH}_3\text{CHCHCOOAg}$, and 0.021wt% for $\text{CH}_3\text{-(CH}_2)_4\text{CHCHCOOAg}$), these silver salts can be obtained as a precipitate by mixing silver nitrate solution with an aqueous solution of sodium carboxylate, which was prepared beforehand by neutralization of the corresponding carboxylic acid with sodium hydroxide, followed by repeated washing with water to remove the resultant sodium nitrate.

The solid-liquid phase diagrams were determined in the following manner. A sample solution (about 1.0-1.5g) was prepared by weighing out water and a concentrated mother solution of a tetrabutylammonium carboxylate; it then was sealed in a small glass ampoule. The mother solutions were prepared by concentrating dilute aqueous solutions, prepared by the method above mentioned, to 60-70 wt% using a rotary evaporator. The concentration of the mother solution was determined by a titration method using a standard tetraphenylborate solution.³⁾ Each ampoule 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 ampoule was slowly warmed (at the rate of about 0.5°C per hour) with vigorous shaking in a constant temperature bath. The temperature at which the solid phase completely disappeared was accurately determined and plotted against the concentration of the solution.

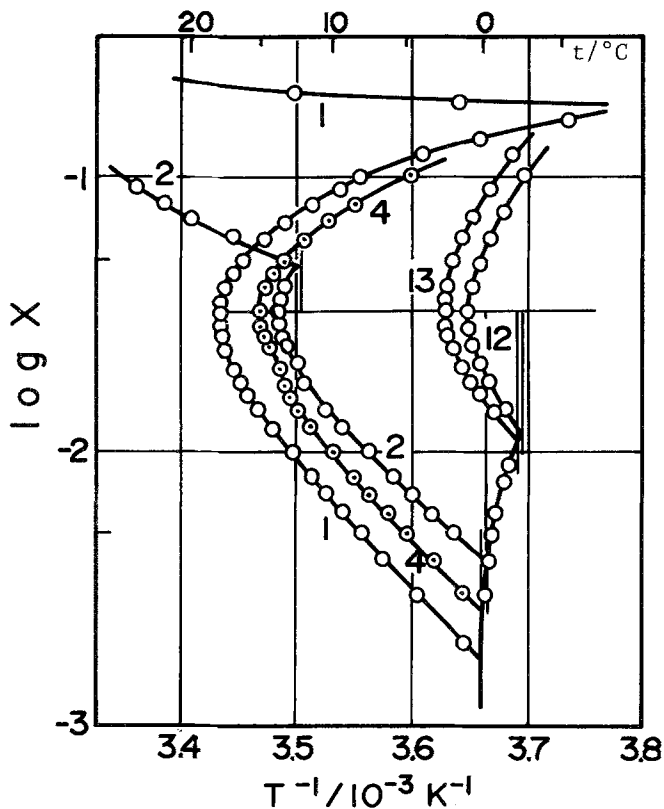


Figure 1. Solid-liquid phase diagrams for water - $(n\text{-C}_4\text{H}_9)_4\text{NOOCR}$ systems. The number attached to each curve stands for the same salt as the one listed in TABLE I. The congruent composition corresponds to the hydrate with hydration number 30.

3. RESULTS

The solid-liquid phase diagrams for tetrabutylammonium unsaturated carboxylate-water binary systems are shown in Figures 1 and 2. In these figures 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. Because of the similarity of the data with one another, some of the results are not shown in these figures.

These figures clearly show that these carboxylates can form clathrate-like hydrates. The presence of these 13 hydrates is newly confirmed in this study. All the melting points and hydration numbers, determined from each congruent melting point and congruent composition, are summarized in TABLE I and those for the carboxylates with the corresponding saturated alkyl groups are given in parentheses.¹⁾ Although the congruent points can clearly be determined by the observation of the dissolution behavior of ampoules at temperatures 0.1–0.2°C below the highest dissolution temperature, the possibility of the formation of a

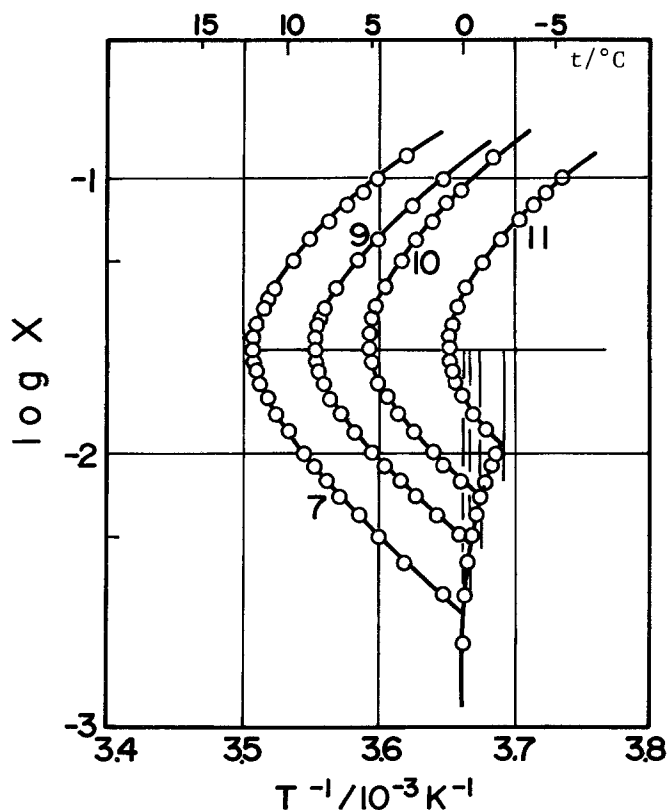


Figure 2. Solid-liquid phase diagrams for water - $(n\text{-C}_4\text{H}_9)_4\text{NOOCR}$ systems. The number attached to each curve stands for the same salt as the one listed in TABLE I. The congruent composition corresponds to the hydrate with hydration number 39.

hydrate with different hydration number is not necessarily deniable since the peaks in these phase diagrams are relatively broad as compared with other systems examined earlier!¹⁾ Especially, there is a high possibility that methacrylate (salt 2 in TABLE I) and vinyl acetate (salt 4) can form a hydrate with hydration number around 39 and that 3-methyl crotonate (salt 6), 2-hexenoate (salt 9), and 3-hexenoate (salt 10) can form hydrates with hydration number around 30. These hydrates are not listed in TABLE I since they are not the stable phases and their exact melting points cannot be determined from the phase diagrams.

TABLE I. Melting points and hydration numbers of the clathrate-like hydrates formed by a series of tetrabutylammonium unsaturated carboxylates $(n-C_4H_9)_4NOOCR$. Similar data for the hydrates of the corresponding saturated carboxylates are given in parentheses.

No.	R	Mp/°C	Hydration number
1	CH ₂ =CH-	17.9(18.0)	30±1(30±1)
2	CH ₂ =C(CH ₃)-	13.6(9.8)	30±2(30±1)
3	CH ₃ CH=CH-	16.9(17.0)	30±1(31±1)
4	CH ₂ =CHCH ₂ -	15.0(17.0)	30±1(31±1)
5	CH ₃ CH=C(CH ₃)-	10.1(7.7)	39±1(40±1)
6	CH ₃ C(CH ₃)=CH-	11.0(11.3)	39±2(39±1)
7	CH ₃ CH ₂ CH=CH-	11.9(10.6)	38±2(40±1)
8	CH ₂ =CH(CH ₂) ₂ -	8.0(10.6)	40±1(40±1)
9	CH ₃ (CH ₂) ₂ CH=CH-	8.2(3.4)	39±2(40±1)
10	CH ₃ CH ₂ CH=CHCH ₂ -	5.2(3.4)	39±2(40±1)
11	CH ₃ CH=CHCH=CH-	0.9(3.4)	39±2(40±1)
12	CH ₃ (CH ₂) ₄ CH=CH-	1.0(1.3)	30±2(29±2)
13	CH ₃ (CH ₂) ₆ CH=CH-	2.6(2.8)	30±2(31±2)

4. DISCUSSION

In Figure 3, the melting point of the hydrate is plotted against the number of carbon atoms in the main chain of each unsaturated carboxylate anion. The points corresponding to the hydrates of a series of 2-alkenoates are connected by a solid line. An open circle indicates a hydrate with hydration number around 30 and a filled circle indicates the one with hydration number around 39. From this figure it is clear that all the points corresponding to the hydrates of hydration number 39 gather in a limited region (shown by the hatched area). Therefore, we analyze these results by classifying these hydrates into three groups I, II, and III in a similar manner as in the case of the hydrates of saturated carboxylates reported before!¹⁾ These three groups are represented in Figure 3.

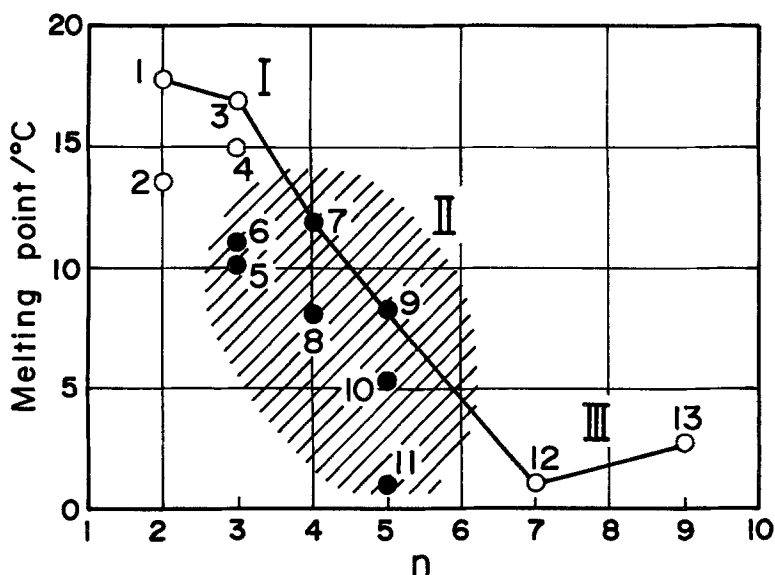


Figure 3. Relationship between the melting points of the hydrates of tetrabutylammonium unsaturated carboxylates $(n\text{-C}_4\text{H}_9)_4\text{NOOCR}$ and the number of carbon atoms (n) in the main chain of R. The number attached to each point stands for the same carboxylate as the one listed in TABLE I.

The group I hydrates are formed by the carboxylates with $\text{R}=\text{CH}_2\text{CH}$, $\text{CH}_2\text{C}(\text{CH}_3)$, CH_3CHCH , and CH_2CHCH_2 and have hydration numbers around 30. These hydrates are fairly stable as compared with those belonging to the other groups. The fact that the hydration number of these hydrates is around 30, just as the hydrates of saturated carboxylates having such short alkyl chains as CH_3 , C_2H_5 , $n\text{-C}_3\text{H}_7$, $i\text{-C}_3\text{H}_7$, and $t\text{-C}_4\text{H}_9$, suggests that the crystal structure of the group I hydrate is isomorphous with that of a well-known tetrabutylammonium fluoride hydrate²⁾ by the same reason as discussed in the previous paper.¹⁾ Therefore, such alkyl groups as $\text{CH}_2\text{CH-}$, $\text{CH}_2\text{C}(\text{CH}_3)\text{-}$, $\text{CH}_3\text{CHCH-}$, and $\text{CH}_2\text{CHCH}_2\text{-}$ seem to be located in a pentagonal dodecahedron, which exists in a gap between the arrangement of larger polyhedra (tetraikaidecahedra and/or pentakaidcahedra 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 gas.

It is interesting to note that (1) from the comparison of the melting point of the acrylate (salt 1 in TABLE I) hydrate to that of the methacrylate (salt 2) hydrate, a methyl group attached to the carbon atom of 2-position causes a considerable distortion in the hydrogen-bonded water framework as found in the case of saturated carboxylate hydrates¹⁾ and (2) the difference in the melting points between the crotonate (salt 3) hydrate and the vinyl acetate (salt 4) hydrate suggests that the decrease in the number of hydrogen atoms attached to the

carbon atom of 2-position contributes to high stability of the hydrate.

The group II hydrates include all the hydrates with the hydration number of 39. They are formed exclusively by all the carboxylates with $R=C_4$ (salts 5-8) and $R=C_5$ (salts 9-11). Generally, the hydrates of $R=C_5$ are less stable than those of $R=C_4$. The large hydration number, 39, as compared with that of the group I hydrate, 30, suggests that the crystal structure of the group II hydrate is essentially the same as that of the tetrabutylammonium benzoate hydrate,⁵⁾ in which the benzoate anion is surrounded by a large polyhedron like tetrakaidecahedron and pentakaidcahedron. The instability of the hydrates of $R=C_5$ may simply be explained by the fact that the C_5 -chain is a little too long to be accommodated stably within such a framework. It is interesting to note that the same structural effect of the alkyl chain of the carboxylate anion on the stability of the hydrate found for the group I hydrates can also be seen in the group II hydrates: (1) the melting point of the 3-methyl crotonate (salt 6, 11.0°C) hydrate is a little higher than that of the tigrate (salt 5, 10.1°C) hydrate, indicating a distortion effect of the methyl group attached to the carbon atom of 2-position; (2) a comparison of the melting points between the 2-pentenoate (salt 7, 11.9°C) hydrate and the 4-pentenoate (salt 8, 8.0°C) hydrate or between the 2-hexenoate (salt 9, 8.2°C) hydrate and the 3-hexenoate (salt 10, 5.2°C) hydrate clearly shows that the decrease in the number of hydrogen atoms attached to the carbon atom of 2-position contributes to high stability of the hydrate.

The group III hydrates are the hydrates with hydration numbers around 30 and are formed by the carboxylates with long alkyl chains like $R=C_7H_{13}$ and $R=C_9H_{17}$. The formation of a similar type of hydrate has also been confirmed for a series of saturated carboxylates with long alkyl chains.¹⁾ From the fact that (1) the hydration number is around 30, (2) the melting points are relatively low, and (3) such long alkyl chains as C_7H_{13} and C_9H_{17} cannot be accommodated within a single pentagonal dodecahedron, the possible crystal structure of the group III hydrates would be that they were isomorphous with a distorted tetrabutylammonium fluoride hydrate and the long alkyl chain of the carboxylate anion penetrated into two (or three) pentagonal dodecahedra, which are face-sharing with each other.

In Figure 4, the melting points of the hydrates of the tetrabutylammonium unsaturated carboxylates are plotted against those of the corresponding saturated carboxylates reported before.¹⁾ Thus, the straight line drawn at an angle of 45° with both axes means the case where the melting points of the hydrates are independent of the presence of a double bond in the alkyl chain of the carboxylate anions. The farther the point deviates upward from the straight line the more stable the hydrate of an unsaturated carboxylate is, and vice versa.

The effects of the presence of a double bond in a carboxylate anion on the stability of its hydrate are summarized as follows:

(1) In the hydrates of the salts 1, 3, 6, 12, and 13, the presence of the double bond has virtually no effect on the stability of these hydrates, suggesting that unfavorable effect caused by the decreased chain flexibility is almost cancelled out by a favorable effect arising from the decrease in the number of hydrogen atoms attached to the car-

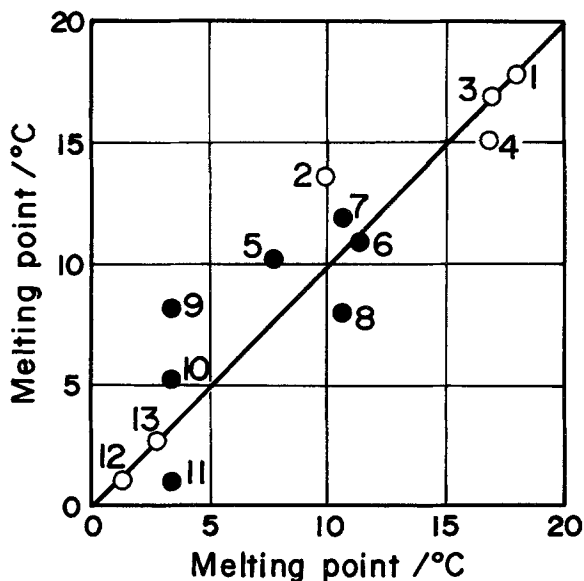


Figure 4. Relationship between the melting points of the tetrabutylammonium unsaturated carboxylates(ordinate) and those of the tetrabutylammonium saturated carboxylates(abscissa). The number attached to each point stands for the same carboxylate as the one listed in TABLE I.

bon atom of 2-position. The latter favorable effect clearly contributes to the stabilization of the hydrates of the salts 2, 5, 7, and 9.

(2) The instability found for the hydrates of the salts 4 and 8 will be due to the presence of a double bond at the end of the alkyl chain since a rotational degree of freedom of the two hydrogen atoms attached to the terminal carbon atom is restricted, causing a distortion on the hydrogen-bonded water framework.

(3) In the hydrates of the salts with $R=C_5$, their stability is more sensibly affected by the modification of C_5 -chain than in any other hydrates since the C_5 -chain itself is, from the first, a little too long to be accommodated stably within a water framework as pointed out above. Thus, the increased stability in the hydrate of salt 10 will be ascribed to a slight shortening of the alkyl-chain length by the introduction of a double bond and instability found for the hydrate of salt 11 will be due to the decreased chain flexibility caused by the presence of two double bonds.

5. REFERENCES

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