[March, 1987] © *1987 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***60***, *839—843 (1987)*

Hydrates of Organic Compounds. XI. Determination of the Melting Point and Hydration Numbers of the Clathrate-Like Hydrate of Tetrabutylammonium Chloride by Differential Scanning Calorimetry

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(Received July 19, 1986)

A thermal analytic method using a differential scanning calorimeter has been applied to binary mixtures of water with tetrabutylammonium chloride. It has been found that this method can give the same results concerning the melting point (15.2 °C) and hydration numbers (around 30) of the clathrate-like hydrate of tetrabutylammonium chloride as those determined phase-diagrammatically. The apparent enthalpy of fusion of water which forms hydrogen-bonded water lattice in the clathrate-like hydrate has been observed to be 5.47 kJ mol^{-1}, which is comparable with 5.20 kJ mol^{-1} determined by the direct calorimetric measurements of enthalpy of solution of the hydrate in water. It has been concluded that the proposed method can be applicable to many similar types of systems, including systems forming a hydrate which decomposes incongruently.

In previous papers the formation of clathrate-like hydrates of tetrabutylammonium salts which have various types of anions (inorganic anions,[1,2]) saturated and unsaturated carboxylate anions,[3-6]) dicarboxylate anions,[7]) and alkanesulfonate anions[8])) has been reported. In these investigations the confirmation of the formation of a hydrate and the determination of melting points and of hydration numbers of the hydrates were made by examining a solid-liquid phase diagram of a binary mixture of a tetrabutylammonium salt with water. The phase diagram was obtained by an ampoule method: the temperature at which the solid phase, formed by cooling a sample solution sealed in an ampoule, completely dissolved was measured; and this temperature was plotted against the concentration of the solution. The ampoule method is one of the most suitable methods since the solid-liquid mixture is thermostated at the desired temperature for sufficient time to establish a solid-liquid phase equilibrium. However, this ampoule method cannot be applied to systems either having extremely high viscosities, as in the case of aqueous solutions containing polymeric ions, or being colored.

In this paper a thermal analytic method using a differential scanning calorimeter has been proposed as an alternative way of confirming the formation of a clathrate-like hydrate as well as of determining a melting point and hydration numbers of the hydrate. The validity of the method has been confirmed by comparing the results concerning the properties of the clathrate-like hydrate of tetrabutylammonium chloride with those obtained in previous investigations.[1,9,10])

Experimental

An aqueous solution of tetrabutylammonium chloride was prepared by neutralization of an aqueous solution of tetrabutylammonium hydroxide with an aqueous solution of hydrochloric acid. The tetrabutylammonium hydroxide solution was prepared by the same procedure as mentioned in a previous paper.[8]) The concentration of the tetrabutylammonium chloride was determined by measuring the amount of tetrabutylammonium cation by titration with a sodium tetraphenylborate solution which was standardized by pure tetrabutylammonium iodide.

The differential scanning calorimeter used was the model DSC 10 with SSC 580 thermal controller manufactured by Seiko Instruments and Electronics Ltd. Sample solutions (about 15 mg) at various concentrations were sealed in a 15 µl aluminum pan. The enthalpy changes per unit time (DSC signal) were measured either by cooling or by heating the sample as slowly as possible (usually at the rate of 0.5 °C per minute). An empty 15 µl aluminum pan was used as a reference. The observed enthalpy changes were standardized by the enthalpy of fusion of ice, i.e., 6.0095 kJ mol^{-1}.[11])

Results and Discussion

An example of the DSC curves on cooling the tetrabutylammonium chloride aqueous solutions at various concentrations is illustrated in Fig. 1. The DSC curves on heating the same solutions are shown in Fig. 2. The concentration of the tetrabutylammonium chloride is expressed by the mole fraction X. As is seen in Figs. 1 and 2, except for the concentrated solution of X=0.050, two kinds of peaks are observed in both cooling and heating processes: the first-step solidification (shown by h in Fig. 1) occurs at −3—−15 °C depending upon the concentration of the salt and the second-step solidification (shown by i in Fig. 1) at −18—−20 °C; and the first-step melting (shown by i in Fig. 2) occurs at around 0 °C and the second-step melting (shown by h in Fig. 2) at 5—15 °C depending upon the concentration of the salt. From the facts that (1) supercooled pure water usually freezes at around −20 °C, (2) the area of the peak i in Figs. 1 and 2 decreases with increasing the concentration of the salt, and (3), on the contrary, the area of peak h in both figures increases with increasing the concentration of the salt, it can be concluded that the peaks indicated by i in both figures are related to an ice phase and, therefore, the peaks indicated by h in both figures are related to a hydrate phase. The disappearance of the peak i in the X=0.050 solution indicates that all the water molecules participate in the formation of the hydrate, i.e., the concentration X=0.050 corresponds to the one which is larger than the congruent composition of the hydrate. It is interesting to note that for the X=0.033 solution small peaks i are observed. This suggests that the congruent composition of the hydrate is close to X=0.033. Firstly, the thermal behavior of the solutions of $X\leqq0.033$ are discussed in the following sections (1) and (2), and those of the solutions of $X>0.033$ are briefly discussed in section (3).

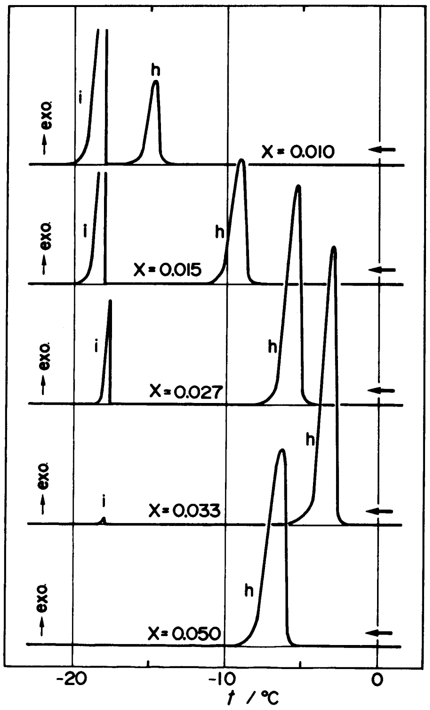

Fig. 1. The DSC curves on cooling for aqueous solutions of tetrabutylammonium chloride at various mole fractions.

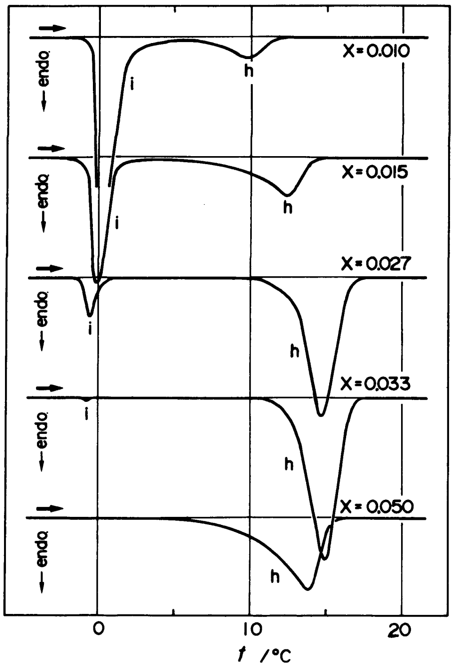

Fig. 2. The DSC cuives on heating for the same solutions as shown in Fig. 1.

(1) Determination of the Hydration Numbers of the Clathrate-Like Hydrate of Tetrabutylammonium Chloride. Although two peaks i and h in the cooling processes (Fig. 1) can be completely separated from each other, these two in the heating processes (Fig. 2) cannot always be separated from each other especially in the solutions of $X<0.02$, as is partly seen in Fig. 2. Therefore, in order to know the enthalpy changes due to the melting of ice and of the hydrate separately, the following two enthalpy changes (ΔH_1 and ΔH_2) have been measured by taking advantage of the complete separation of the two peaks (i and h) in the cooling process. These two enthalpy changes are illustrated in Fig. 3 where ΔH_1 is the enthalpy change when heated after the sample solution is completely solidified by cooling below −20 °C (process (a) in Fig. 3). The ΔH_2 is the enthalpy change when heated after the sample solution is partially solidified by cooling the sample down to the temperature at which the hydrate phase is completely solidified but the water which does not participate in the formation of the hydrate remains in a liquid state (process (b) in Fig. 3). The observed values of ΔH_1 and of ΔH_2 are listed in Table 1 together with other data explained below. These values are averages of three to five measurements and the limit of error attached to each value is estimated not only by

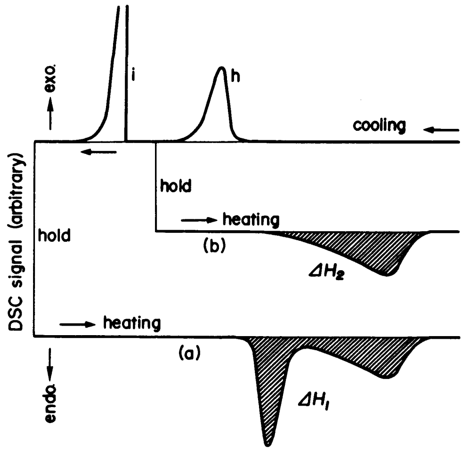

Fig. 3. The measuring processes of the two types of enthalpy changes ΔH_1 and ΔH_2.

the deviations from the mean value but also by the error arising from the procedure of determining the areas of the DSC curves.

The physical meaning of both ΔH_1 and ΔH_2 is not necessarily clear for the following reasons: (1) The composition of the liquid phase co-existing with the hydrate solid which is formed in the first-step cooling (peak h in Fig. 1) is not obvious since this mixture is not in an equilibrium state; and (2) for dilute solutions, especially when X is smaller than 0.005, the observed values of ΔH_2 vary from experiment to experiment, suggesting that the solid phase formed in the first-step cooling has some irregularity. If we neglect all the irregularities concerning the structure and chemical composition of the hydrate solid, ΔH_1 and ΔH_2 can approximately be expressed by the following relations:

$$\Delta H_1 = (n_0 - mn_1)\Delta H_{f,\mathrm{ice}} + n_1\Delta H_{f,\mathrm{hyd}} + \Delta H_{\mathrm{M}}(n_1), \tag{1}$$

$$\Delta H_2 = n_1'\Delta H_{f,\mathrm{hyd}} + \Delta H_{\mathrm{M}}(n_1'), \tag{2}$$

in which n_0 and n_1 are the total number of moles of water and of tetrabutylammonium chloride contained in a sample. $\Delta H_{f,\mathrm{ice}}$ and $\Delta H_{f,\mathrm{hyd}}$ are the molar enthalpy of fusion of ice and of the hydrate expressed by a formula $(n\text{-}C_4H_9)_4NCl\cdot mH_2O$, in which m is the hydration numbers, and n_1' is the number of moles of the hydrate formed in the first-step cooling. The $\Delta H_{\mathrm{M}}(n_1)$ is the total enthalpy of mixing of $n_0 - mn_1$ moles of water with n_1 moles of the hydrate melt. Similarly $\Delta H_{\mathrm{M}}(n_1')$ is the total enthalpy of mixing of the liquid phase co-existing with the hydrate solid formed in the first-step cooling with n_1' moles of the hydrate melt.

The present results cannot directly be analyzed by these two equations since there is no information about the values of n_1' as well as of the enthalpies of mixing. However, for solutions whose concentration is not extremely low, it can be assumed that n_1' is equal to n_1, at least as a first approximation, since according to the phase-diagrammatic experiment for the same system the eutectic composition of the solution which is in equilibrium with the $(n\text{-}C_4H_9)_4NCl$ hydrate solid+ice mixture is as low as $X=0.002$.[9] This assumption means that the liquid phase which is co-existing with the hydrate solid formed in the first-step cooling is pure water instead of a dilute aqueous solution of $(n\text{-}C_4H_9)_4NCl$. Accordingly it leads to the simple relation that the enthalpy of mixing terms in Eqs. 1 and 2 become identical. Therefore, from Eqs. 1 and 2, the hydration numbers, m, of the hydrate can be expressed by the following relation:

$$m = \frac{1}{n_1}\left\{n_0 - \frac{\Delta H_1 - \Delta H_2}{6.0095\times 10^3}\right\}, \tag{3}$$

in which both ΔH_1 and ΔH_2 are expressed in J unit and $\Delta H_{f,\mathrm{ice}} = 6.0095\times 10^3$ J is used, which is equal to the molar enthalpy of fusion of ice I at 0 °C.[11]

The calculated values of m, together with the values of n_0 and of n_1 for each sample solution, are listed in Table 1. It is interesting to note that the calculated hydration numbers are around 30, in good agreement with the value 30±1 determined from phase diagrammatic experiments.[9] This suggests that Eq. 3 is appropriate to the determination of the hydration numbers of a clathrate-like hydrate at least as a first approximation. The small value of m obtained for the $X=0.005$ solution indicates that the assumption made to obtain Eq. 3 is not appropriate to such a dilute solution.

It should be noted that the hydration numbers of the hydrate can be determined from the measurements of both ΔH_1 and ΔH_2 for some solutions at any concentrations except for very dilute or very concentrated solutions. Furthermore this method can also be applied to the systems forming a hydrate which decomposes incongruently if the two enthalpy changes, ΔH_1 and ΔH_2, can be measured for the solutions whose concentrations are lower than the composition corresponding to its incongruent melting point.

In Fig. 4, the apparent enthlpy change for one mole of water, $\Delta H_1/n_0$, and the apparent enthalpy change

Table 1. Dissolution Temperature t, Enthalpy Changes ΔH_1 and ΔH_2, and Calculated Hydration Numbers m for the Tetrabutylammonium Chloride Clathrate-Like Hydrate

X[a)]	n_0[a)] / 10^{-4} mol	n_1[a)] / 10^{-5} mol	t / °C	ΔH_1 / J	ΔH_2 / J	m
0.005	7.8712	0.3958	6.4	4.53±0.12	0.43±0.04	26.5±5.3
0.010	7.0441	0.7124	10.2	3.95±0.08	0.98±0.03	29.5±2.0
0.015	7.0666	1.0756	12.5	3.85±0.11	1.66±0.05	31.8±1.9
0.020	6.4807	1.3259	14.3	3.45±0.08	2.11±0.05	32.1±1.2
0.027	5.3167	1.4759	14.8	2.85±0.05	2.39±0.05	30.8±0.8
0.033	5.5761	1.9230	15.2	3.05±0.04	3.05±0.04	29.0±0.5
0.040	5.5580	2.3234	15.0	2.78±0.05	2.78±0.05	—
0.050	4.5064	2.3466	14.2	1.69±0.06	1.69±0.06	—

a) Notations X, n_0, and n_1 are explained in the text.

for one mole of water which forms hydrogen-bonded networks in the hydrate solid, $\Delta H_2/mn_1$, are plotted against X. An exact analysis of both curves is difficult due to the lack of information about the concentration dependence of the enthalpies of dilution and temperature dependence of the enthalpies of fusion and of dilution for both water and the hydrate. However, it is interesting to note that (1) the congruent composition of the hydrate, i.e., the hydration numbers, can also be determined by finding the concentration at which both curves coincide since the relations $\Delta H_1=\Delta H_2$ and $n_0=mn_1$ hold at the congruent composition. It is also notable that the value of $\Delta H_2/mn_1$ (or $\Delta H_1/n_0$) at the congruent composition is equal to 5.47 kJ mol^{-1}, in fair agreement with the value of 5.20 kJ mol^{-1} at 10 °C estimated from direct calorimetric measurements of the enthalpies of solution of the tetrabutylammonium chloride hydrate in water.[10]

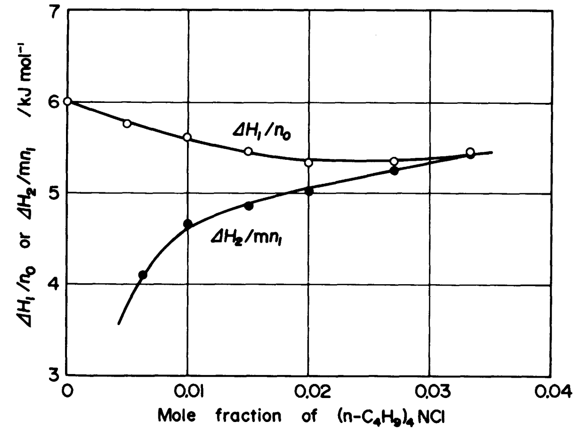

Fig. 4. Concentration dependence of the two apparent enthalpy changes, $\Delta H_1/n_0$ and $\Delta H_2/mn_1$, for tetrabutylammonium chloride–water system. The physical meanings of ΔH_1 and ΔH_2 are shown in Fig. 3, n_0 and n_1 are the total number of moles of water and of the salt contained in a sample solution, and m is the hydration numbers of the hydrate.

(2) Determination of the Melting Point of the Clathrate-Like Hydrate of Tetrabutylammonium Chloride. The melting point of the hydrate can be determined by finding the highest dissolution temperature for solutions at various concentrations. The dissolution temperature is that at which the solid phase completely dissolves when the solidified sample is gradually heated. Although this temperature is measured with the naked eye in an ordinary ampoule method, it can also be determined by the DSC experiments as illustrated in Fig. 5. In the heating process (b) in Fig. 3, the hydrate solid is first heated to a given temperature, t_0 for example, and is held at t_0 for a while. The sample is then further heated to a temperature higher than the presumed melting point. If the dissolution temperature of the sample, t, lies higher than t_0, an additional endothermic enthalpy change can be observed in the reheating process as marked A in Fig. 5. Thus the exact dissolution temperature can be determined by finding the lowest temperature t_0, as t_0'' in Fig. 5, for which no additional enthalpy change (peak A) is observed. It has been found that the dissolution temperature thus determined is practically equal to the temperature at which the heating DSC curves for the hydrate (the (b) process in Fig. 3) show a minimum: i.e., the temperature at which d(DSC signal)/dT=0. The dissolution temperatures so observed are listed in Table 1 for each solution. In Fig. 6, this temperature is compared with that determined by the ampoule method reported earlier.[9] This figure (i.e., a solid-liquid phase diagram) clearly indicates that the dissolution

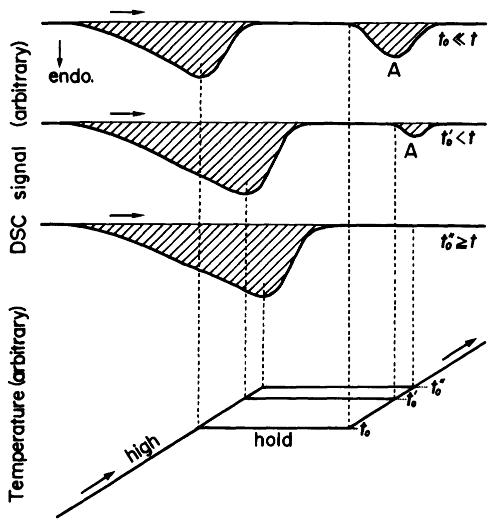

Fig. 5. The measuring process of the dissolution temperature, t, of the hydrate.

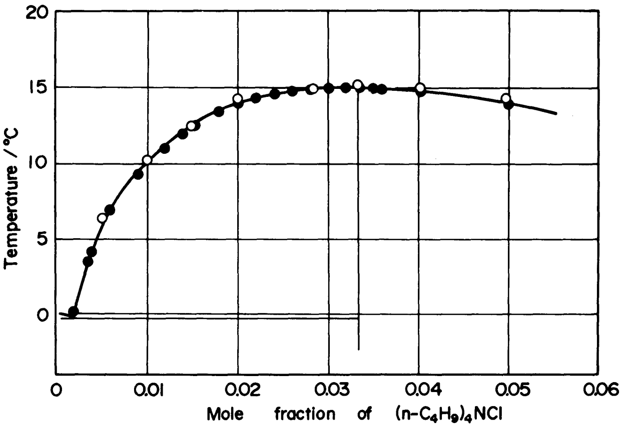

Fig. 6. The solid-liquid phase diagram for tetrabutylammonium chloride–water system determined by the dissolution temperatures. ○: values determined by the present DSC measurements; and ●: values determined by an ampoule method (Ref. 9).

temperature can be exactly determined by the DSC measurements. As is obvious from Table 1 and Fig. 6, a value of X=0.033 gives the maximum dissolution temperature (i.e., the melting point of the hydrate) of 15.2 °C. This indicates not only that this observed melting point is in good agreement with the 15.0 °C, determined phase-diagrammatically[9] but also that X=0.033 corresponds to the hydration numbers of 29, in good agreement with the result obtained in section (1).

In conclusion, through the discussions in the sections (1) and (2), the present thermal analytic method can give the same results concerning the nature of the clathrate-like hydrate of tetrabutylammonium chloride as those obtained phase-diagrammatically. Since the fundamental principle of the present method is not limited to an aqueous solution of the tetrabutylammonium chloride only, this method may be applicable to many similar types of systems, including the systems forming a hydrate which decomposes incongruently, so long as the two enthalpy changes, ΔH_1 and ΔH_2, can be measured.

(3) Thermal Properties of the Solutions at Higher Concentrations Than the Congruent Composition. Finally, the thermal behavior of the solutions above X=0.033 is discussed briefly. The behavior of the DSC signals is exemplified for the solution of X=0.050 in Figs. 1 and 2. The measured enthalpy changes are also listed in Table 1 for two solutions with X=0.040 and 0.050. The two enthalpy changes ΔH_1 and ΔH_2 inevitably become identical since the enthalpy change due to the melting of ice phase is not present for these concentrated solutions (Fig. 1 and 2). If we assume that all the water molecules participate in the formation of the hydrate solid having the hydration numbers around 30 and further that the enthalpy of fusion of these water molecules is equal to 5.47 kJ mol^{-1} estimated in the above discussion, the expected values of ΔH_1 (or ΔH_2) become 3.04 J for the X=0.040 solution and 2.47 J for the X=0.050 solution, respectively. The observed values listed in Table 1, 2.78 J for the X=0.040 solution and 1.69 J for the X=0.050 solution, are apprecially small as compared with those expected values, especially for the X=0.050 solution. At present exact thermal analyses are impossible because of a lack of information concerning the state of the phases existing in such concentrated solutions.

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

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