Hydrates of Organic Compounds. XIII. The Confirmation of the Formation of Clathrate-Like Hydrates of Tetrabutylammonium and of Tetraisopentylammonium Polyacrylates

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A thermal analytic method using a differential scanning calorimeter has been applied to aqueous solutions of a series of tetraalkylammonium polyacrylates (($R_4NOOCCHCH_2)_n$; R=CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, n-C_5H_{11}, and i-C_5H_{11}). It was found that only tetrabutylammonium polyacrylate and tetraisopentylammonium polyacrylate could form stable hydrates having a large number of moles of water per single $R_4NOOCCHCH_2$ unit of the polyacrylates (hydration numbers). The melting points and hydration numbers of these two hydrates were 11.2 °C, 30±1 for the tetrabutylammonium polyacrylate hydrate and 19.5 °C, 42±2 for the tetraisopentylammonium polyacrylate hydrate, respectively. Judging from the melting points, hydration numbers, and the concentration dependence of the dissolution temperatures, these hydrates were regarded as clathrate-like. The tetrabutylammonium polyacrylate hydrate seems to be iso-structural with (n-$C_4H_9)_4NF$ hydrate and the tetraisopentylammonium polyacrylate hydrate with (i-$C_5H_{11})_4NF$ hydrate.

A single-crystal X-ray examination by Jeffrey and his coworkers on the hydrates of tetraalkylammonium salts such as (n-$C_4H_9)_4NF$,[1] (n-$C_4H_9)_4NOOCC_6H_5$,[2] and (i-$C_5H_{11})_4NF$,[3] showed that these hydrates were clathrate-like hydrates similar to the so-called gas hydrates.[4] The water structure is a hydrogen-bonded framework and is essentially a regular arrangement of polyhedra like pentagonal dodecahedra, tetrakaidecahedra, and pentakaidecahedra. The latter two polyhedra enclose either a n-C_4H_9 or a i-C_5H_{11} group of the tetraalkylammonium cations, whereas pentagonal dodecahedra are empty. Fluoride ion and oxygen atoms of carboxylate anion are hydrogen-bonded to the water frameworks and form part of the polyhedral structure.

Although the tetraalkylammonium cation which can form a clathrate-like hydrate is almost exclusively limited either to tetrabutylammonium ion or to tetraisopentylammonium ion,[5–7] various types of anions are permissble. Of these anions, carboxylate anions are of interest since they can extend the diversity of the clathrate-like hydrates of tetraalkylammonium salts due to the variation of the alkyl groups of the carboxylate anions. The formation of a clathrate-like hydrate of tetrabutylammonium carboxylates has been confirmed for many carboxylates.[2,3,5,8–12] Experimental results found so far are briefly summarized as follows: (1) a series of tetrabutylammonium carboxylates, (n-$C_4H_9)_4NOOCR$, with R ranging from CH_3 to n-$C_{10}H_{21}$ can form clathrate-like hydrates whose hydration numbers are around 30;[10,12] and (2) a series of tetrabutylammonium dicarboxylates, $[(n\text{-}C_4H_9)_4N]_2(OOC(CH_2)_nCOO)$ (n=0—8), can also form clathrate-like hydrates with hydration numbers around 60 and the salt of n=3 forms the most stable hydrate whose melting point is 20.2 °C.[9]

The crystal structure of these carboxylate and dicarboxylate hydrates was assumed to be iso-structural with that of the (n-$C_4H_9)_4NF$ hydrate[1] from the fact that the hydration numbers (about 30 for one (n-$C_4H_9)_4N^+$ cation) and unit cell dimensions for some of the hydrates[12] are almost identical with those of the (n-$C_4H_9)_4NF$ hydrate. This speculation also means that the alkyl groups of carboxylate anions and methylene chains of dicarboxylate anions are enclosed in vacant pentagonal dodecahedra.

From such a versatile availability of vacant pentagonal dodecahedra and from the fact that, for dicarboxylate salts, the $-(CH_2)_3-$ methylene chain is the most suitable chain to form a stable clathrate-like hydrate, the formation of a clathrate-like hydrate of tetrabutylammonium polyacrylate and of tetraisopentylammonium polyacrylate may be anticipated, though such a hydrate has not been known previously.

In this paper, through a thermal analytic method using a differential scanning calorimeter for binary mixtures of a series of tetraalkylammonium polyacrylates (($R_4NOOCCHCH_2)_n$; R=CH_3—n-C_5H_{11}, and i-C_5H_{11}) with water, an extensive study has been carried out in order to confirm the formation of clathrate-like hydrates of teraalkylammonium polyacrylates.

Experimental

Aqueous solutions of sodium polyacrylate and of tetraalkylammonium polyacrylates (($R_4NOOCCHCH_2)_n$; R=CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, n-C_5H_{11}, and i-C_5H_{11}) were obtained by the neutralization of an aqueous solution of polyacrylic acid with aqueous solutions of sodium hydroxide and of the corresponding tetraalkylammonium hydroxide. The aqueous solutions of tetraalkylammonium hydroxides were prepared by reacting tetraalkylammonium iodides with freshly prepared silver hydroxide in water with vigorous shaking, followed by filtration of resulting silver iodide in a CO_2-free atmosphere. Tetrabutylammonium iodide, tetrapentylammonium iodide, and tetraisopentylammonium iodide were synthesized by reacting each trialkylamine with the corresponding alkyl iodide in ethyl acetate and were purified by recrystallization from ethyl acetate–acetone mixture.[7] Other iodides were purchased from the Tokyo Kasei Kogyo Co. and were recrystallized either from ethyl acetate–ethanol mixture or from ethanol. An aqueous solution of polyacrylic acid was purchased from Wako Pure Chemical Industries, Ltd. and was used without further purification. The mean degree of polymerization of polyacrylic acid was estimated to be about 2100 from viscosity measurements of the aqueous solutions of its sodium salt in 1 mol dm^{-3} NaCl solution at 25 °C using the equation proposed by Kagawa et al.[13]

The concentrations of each sample were determined either by measuring the water content using the Karl Fischer titration method on a MK-II apparatus (Kyoto Electronics Manufacturing Co.) for sodium polyacrylate and tetramethyl-, tetraethyl-, tetrapropyl-, and tetrapentylammonium polyacrylates or by measuring the amount of tetraalkylammonium cations by titration with a sodium tetraphenylborate solution which was standardized by pure tetrabutylammonium iodide for tetrabutyl- and tetraisopentylammonium polyacrylates.

The differential scanning calorimeter used was the model DSC-10 with SSC-580 thermal controller, manufactured by Seiko Instruments and Electronics Ltd. Each sample solution (about 15 mg) was sealed in a 15 μl aluminum pan and was either cooled or heated at the rate of 0.5 °C per minute. An empty 15 μl aluminum pan was used as a reference.

Results and Discussion

(1) Thermal Behavior of Aqueous Solutions of Sodium Polyacrylate and of Tetraalkylammonium Polyacrylates. The cooling and heating curves in the differential scanning calorimetry (DSC) for aqueous solutions of sodium polyacrylate (NaPA), tetramethylammonium polyacrylate ($(CH_3)_4NPA$), tetraethylammonium polyacrylate ($(C_2H_5)_4NPA$), tetrapropylammonium polyacrylate ($(n\text{-}C_3H_7)_4NPA$), tetrabutylammonium polyacrylate ($(n\text{-}C_4H_9)_4NPA$), tetrapentylammonium polyacrylate ($(n\text{-}C_5H_{11})_4NPA$) and tetraisopentylammonium polyacrylate ($(i\text{-}C_5H_{11})_4NPA$) are shown as a function of temperature for solutions of X=0.01 in Fig. 1 and of X=0.02 in Fig. 2 (X is the mole fraction of the polyacrylates based on the monomeric unit). It is obvious that in the cooling process steep exothermic peaks in the −15—−20 °C range indicate the solidification of supercooled water, and in the heating process endothermic peaks in the −10—0 °C

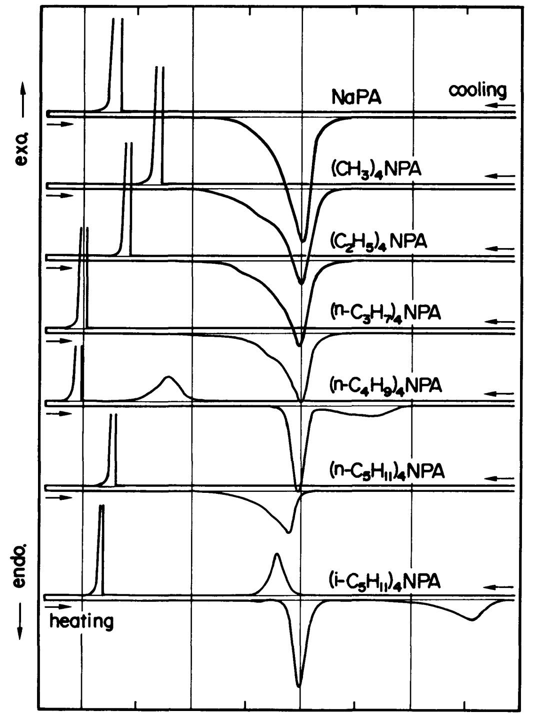

Fig. 1. Temperature dependence of the DSC signals, expressed in an arbitrary unit, for aqueous solutions of sodium polyacrylate (NaPA) and of a series of tetraalkylammonium polyacrylates (R_4NPA; R= CH_3, C_2H_5, $n\text{-}C_3H_7$, $n\text{-}C_4H_9$, $n\text{-}C_5H_{11}$, and $i\text{-}C_5H_{11}$). The mole fraction (X), based on the monomeric unit, is equal to 0.01 for all the solutions.

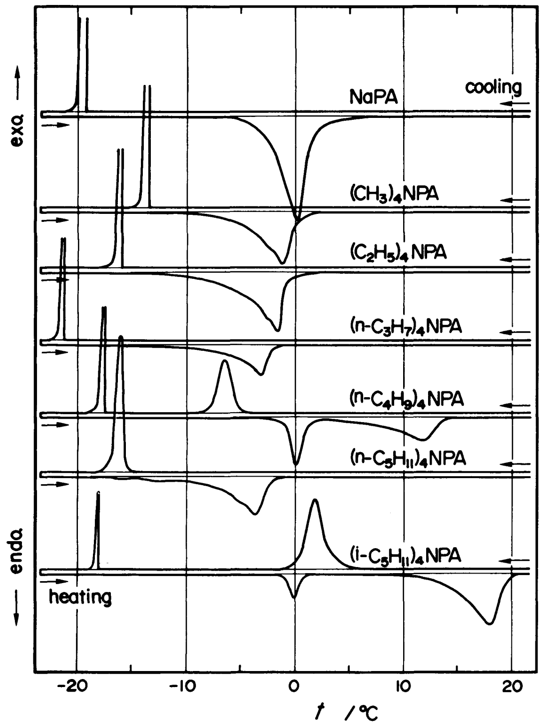

Fig. 2. Temperature dependence of the DSC signals, expressed in an arbitrary unit, for aqueous solutions of sodium polyacrylate (NaPA) and of a series of tetraalkylammonium polyacrylates (R_4NPA; R= CH_3, C_2H_5, $n\text{-}C_3H_7$, $n\text{-}C_4H_9$, $n\text{-}C_5H_{11}$, and $i\text{-}C_5H_{11}$). The mole fraction, based on the monomeric unit, is equal to 0.02 for all the solutions.

range are attributable to the melting of the ice phase.

However, the thermal behavior of $(n\text{-}C_4H_9)_4$NPA and $(i\text{-}C_5H_{11})_4$NPA solutions differs markedly from that of the other five solutions. In these two solutions, besides the peaks due to an ice phase exothermic peak occurs at around −12 °C for X=0.01 and around −7 °C for X=0.02 in the $(n\text{-}C_4H_9)_4$NPA solutions and at around −2 °C for X=0.01 and at around +2 °C for X=0.02 in the $(i\text{-}C_5H_{11})_4$NPA solutions and the endothermic peak occurs at temperatures above 0 °C depending both on the concentration and on the kind of salt. This clearly indicates that another solid phase other than ice is formed in these two systems and further that this solid phase contains some water, i.e., a hydrate, since the areas of both the exothermic peaks due to the solidification of supercooled water and of the endothermic peak due to the melting of the ice phase decrease markedly with increasing concentration of the salt. Further details of these hydrates will be discussed in the following sections.

Finally, the quantities $\Delta H/(6.0095\times10^3 n_0)$ for all the solutions examined are listed in Table 1, where ΔH (J unit) is the total endothermic enthalpy change in the heating process and n_0 is the total number of moles of water contained in each solution and the value 6.0095×10^3 is the molar heat of fusion (J unit) of pure water at 0 °C.[14] This quantity may be regarded as an approximate index of the relative thermal stability of the solid phase as compared with that of pure ice. The values obtained are very small for the X=0.02 solution of $(n\text{-}C_3H_7)_4$NPA and both X=0.01 and X=0.02 solutions of $(n\text{-}C_5H_{11})_4$NPA. At the same time, Figs. 1 and 2 show that the melting processes of the solid phase in these three solutions are completed at lower temperatures than those in the other solutions. These phenomena indicate that the degree of amorphousness of the ice phase formed around the $(n\text{-}C_3H_7)_4$NPA and $(n\text{-}C_5H_{11})_4$NPA molecules remarkably increases.

Table 1. The Quantity $\Delta H/(6.0095\times10^3 n_0)$ for Aqueous Solutions of Sodium Polyacrylate and of Tetraalkylammonium Polyacrylates

Polyacrylate	$\Delta H/(6.0095\times10^3 n_0)$	
	X=0.01	X=0.02
NaPA	0.98	0.99
$(CH_3)_4$NPA	0.96	0.80
$(C_2H_5)_4$NPA	1.00	0.75
$(n\text{-}C_3H_7)_4$NPA	0.82	0.50
$(n\text{-}C_4H_9)_4$NPA	0.88	0.77
$(n\text{-}C_5H_{11})_4$NPA	0.62	0.60
$(i\text{-}C_5H_{11})_4$NPA	0.85	0.87

All the notations are explained in the text. These values are averages of 3—5 measurements.

(2) The Confirmation of the Formation of a Clathrate-Like Hydrate of Tetrabutylammonium Polyacrylate. In a preliminary experiment it was found that when about 10 wt% aqueous solution of $(n\text{-}C_4H_9)_4$NPA was cooled to about −20 °C, a white and powderly solid phase was formed which remained undissolved at 2 °C. This suggests the formation of a solid phase other than ice. The cooling and heating curves for the $(n\text{-}C_4H_9)_4$NPA solutions in various concentrations are shown in Fig. 3 as a function of temperature. The most important characteristic of both the cooling and heating curves is the occurrence of two kinds of peaks except for the solutions whose X's are either very small or very large. The areas of both the exothermic peaks corresponding to the solidification of ice and the endothermic peak corresponding to the melting of ice decrease markedly with increasing concentration and both peaks become very small when X=0.0330. Therefore, the solid phase other than ice seems to be a hydrate whose composition is approximately equal to X=0.0330, i.e., the hydration number of the hydrate is close to 29.

The thermal behavior shown in Fig. 3 shows a striking resemblance to that of the aqueous solutions

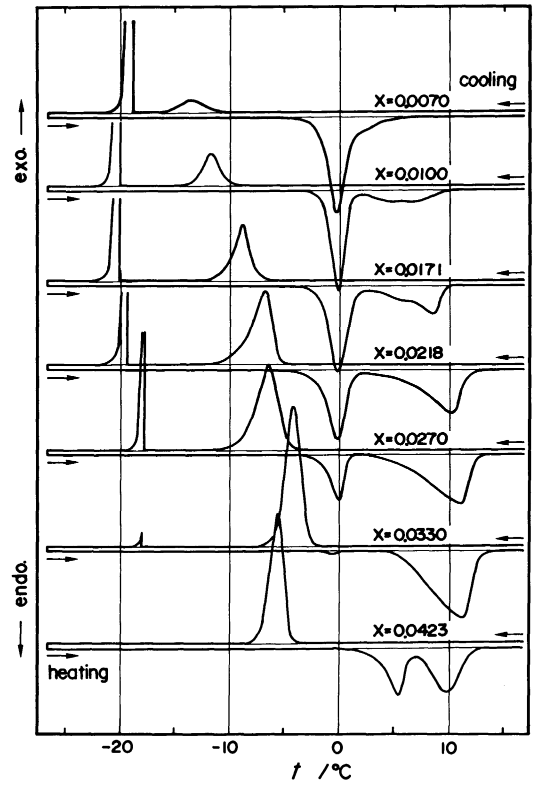

Fig. 3. Temperature dependence of the DSC signals, expressed in an arbitrary unit, for aqueous solutions of tetrabutylammonium polyacrylate ($(n\text{-}C_4H_9)_4$NPA) in various concentrations. The X is the mole fraction of the salt based on the monomeric unit.

of tetrabutylammonium chloride,[15] which is well-known to form a clathrate-like hydrate with hydration numbers around 30.[5,7,16] A thermal analytic procedure for obtaining hydration numbers and melting pont of a hydrate, and for determining the dissolution temperatures by DSC measurements has precisely been discussed in a previous paper.[15] The hydration numbers, m, of a hydrate can approximately be calculated by the following relation for solutions whose X's are equal to or smaller than the congruent composition:

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

in which ΔH_1 (J unit) is the total enthalpy change during the whole heating processes for the solid phases which are solidified both by the first-step and by the second-step solidification; ΔH_2 (J unit) is the enthalpy change in the heating process for the solid phase which is solidified by the first-step solidification process only; n_0 and n_1 are the total number of moles of water and of $(n\text{-}C_4H_9)_4NPA$ based on the monomeric unit, respectively. Some representative values of ΔH_1, ΔH_2, the dissolution temperatures observed, and the calculated hydration numbers m are listed in Table 2, together with some data for the solutions at concentrations higher than X=0.0330. These are briefly discussed in the last part of this section.

All the calculated values of m lie near 30 and the X=0.0330 solution has the highest dissolution temperature of 11.2 °C and almost the same values of ΔH_1 and ΔH_2, indicating that the congruent composition of the hydrate is close to X=0.0330 as observed above. In conclusion, the hydration numbers and the melting point of the $(n\text{-}C_4H_9)_4NPA$ hydrate are determined to be 30±1 and 11.2 °C, respectively. The presence of the $(n\text{-}C_4H_9)_4NPA$ hydrate has not been known previously. From the facts that the hydration numbers of the hydrate are 30±1, and the congruent melting pont is fairly high (11.2 °C), this hydrate seems to have a clathrate-like structure similar to such hydrates as $(n\text{-}C_4H_9)_4NF\cdot30H_2O$ and $(n\text{-}C_4H_9)_4NCl\cdot30H_2O$.[15,16]

The solid-liquid phase diagram for the $(n\text{-}C_4H_9)_4NPA\text{-}H_2O$ binary system, which is depicted by

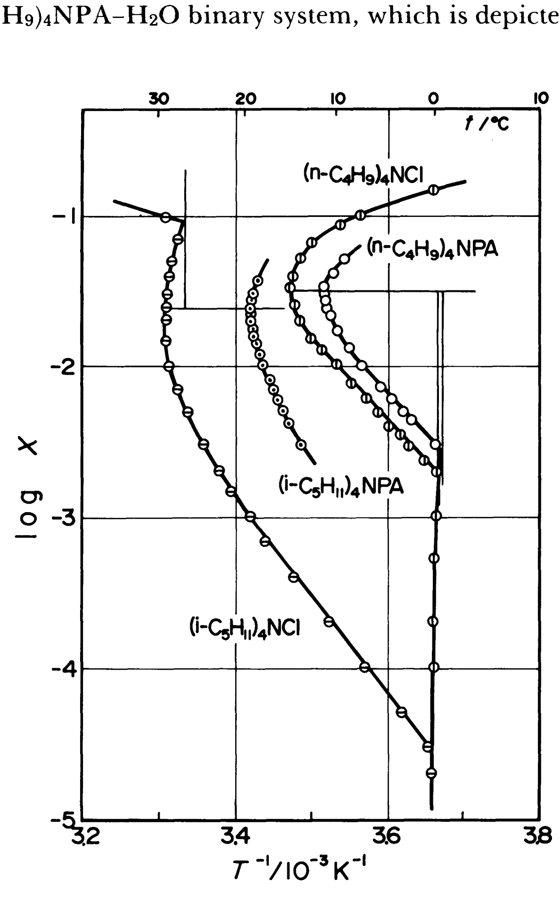

Fig. 4. The solid-liquid phase diagrams for binary systems of tetrabutylammonium polyacrylate ($(n\text{-}C_4H_9)_4NPA$)-water and of tetraisopentylammonium polyacrylate ($(i\text{-}C_5H_{11})_4NPA$)-water determined by the DSC experiments, together with those for binary systems of $(n\text{-}C_4H_9)_4NCl$-water and of $(i\text{-}C_5H_{11})_4NCl$-water determined previously by an ampoule method.[7,16]

Table 2. Dissolution Temperatures t, Enthalpy Changes ΔH_1 and ΔH_2, and Calculated Hydration Numbers m for Aqueous Solutions of Tetrabutylammonium Polyacrylate

X	n_0 / 10^{-4}mol	n_1 / 10^{-5}mol	t / °C	ΔH_1[a] / J	ΔH_2[a] / J	m
0.0070	8.8102	0.6214	5.2	4.81±0.08	0.64±0.03	30.1±2.3
0.0100	7.3641	0.7443	7.1	3.88±0.08	0.83±0.03	30.8±1.9
0.0171	6.9940	1.2153	9.7	3.38±0.05	1.44±0.04	31.0±0.9
0.0218	7.1983	1.6018	10.5	3.35±0.06	1.98±0.05	30.7±0.8
0.0270	6.3237	1.7535	11.0	2.89±0.03	2.26±0.05	30.1±0.5
0.0330	5.1716	1.7649	11.2	2.37±0.03	2.35±0.04	29.1±0.5
0.0423	5.3366	2.3590	10.0	2.31±0.12	1.43±0.10	—
0.0506	4.5584	2.4298	9.0	1.83±0.15	0.26±0.08	—

All the notations are explained in the text.

a) These values are averages of 3—5 measurements.

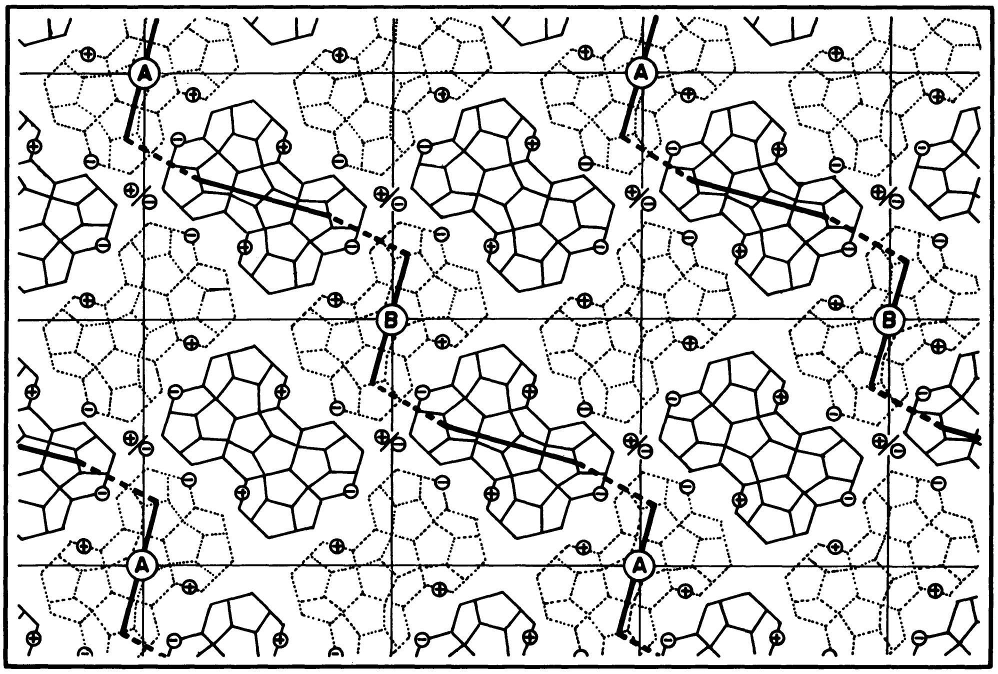

Fig. 5. One of the possible ways for polyacrylate chains (written by bold lines) to be accommodated within the structure which is iso-structural with $(n\text{-}C_4H_9)_4NF$ hydrate. Explanation is given in the text.

plotting the logarithm of the mole fraction X of each solution against their dissolution temperatures after conversion to the reciprocal of the absolute temperature, is shown in Fig. 4, together with that of the $(n\text{-}C_4H_9)_4NCl\text{-}H_2O$ system determined previously by an ampoule method.[16] A striking resemblance of both phase diagrams, especially a similar value of the slope of $-\partial \log X/\partial(1/T)$ in the concentration range between the eutectic composition and the congruent composition, provides another indication for the formation of a clathrate-like hydrate of $(n\text{-}C_4H_9)_4NPA$ similar to that of $(n\text{-}C_4H_9)NCl$. This slope has been proved to be approximately proportional to the hydration number of a hydrate.[17].

Although there is no information about the crystal structure of the $(n\text{-}C_4H_9)_4NPA$ hydrate, the most probable way of accommodating a polyacrylate chain within a water lattice is illustrated in Fig. 5 based on the assumptions that (1) the crystal structure is iso-structural with that of the $(n\text{-}C_4H_9)_4NF$ hydrate[1] and (2) the polyacrylate chain penetrates through associated, vacant pentagonal dodecahedra forming a hydrogen-bonded anionic host structure with water. In this figure only an arrangement of a block of vacant pentagonal dodecahedra in the planes perpendicular to the c-axis is shown. Each block represented by a solid line lies at the level of the $Z=0$ plane and the one represented by a dotted line lies at the level of the $Z=1/2$ plane. The marks ⊕ and ⊖ represent the positions of a nitrogen atom and of a fluorine atom, respectively, in the original $(n\text{-}C_4H_9)_4NF$ hydrate. The C–C main chain of the polyacrylate anion is illustrated by bold lines. The dotted portion of the bold line indicates the shift of the C–C chain between the $Z=0$ and $Z=1/2$ plane by breaking a single hydrogen-bond which connects two blocks of the pentagonal dodecahedra. The distance from position A to B in Fig. 5 is about 45 Å and the monomeric unit chain length of the polyacrylate chain is expected to be slightly shorter than 2.51 Å, which is the longest distance when the C–C chain is fully extended. This is because of the restriction that each carboxyl group must be incorporated within the water framework. Therefore, it will be reasonable to assume that 20 monomeric units of the polyacrylate chain are present between A and B. According to the structural analysis by Jeffrey et al.,[1] there exist 10 pentagonal dodecahedra (i.e., two blocks of pentagonal dodecahedra represented in Fig. 5) and five $(n\text{-}C_4H_9)_4NF$ molecules within a unit cell. Thus the above mentioned 20 units of negative charge are four times larger than the positive charge, leading the conclusion that only a fourth of all the pentagonal dodecahedra are used to accommodate the polyacrylate chain. This may be possible, for instance, if only the pentagonal dodecahedra existing within alternate unit cells arranged in the directions both perpendicular and parallel to the c-axis are used. Figure 5 is drawn according to this view.

In Fig. 6 two apparent quantities, $\Delta H_1/n_0$ and

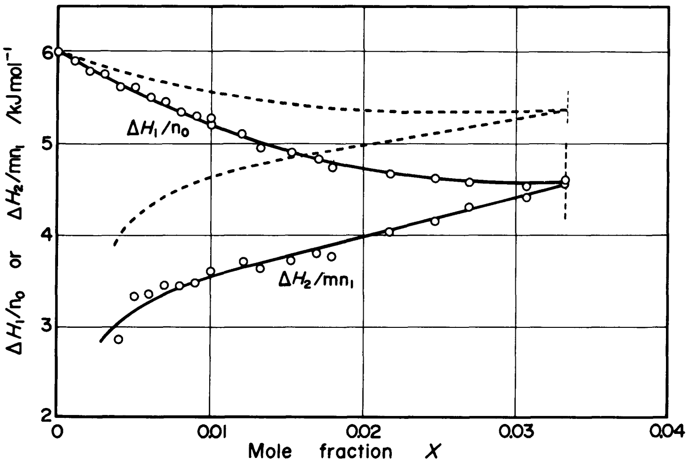

Fig. 6. The concentration dependence of the apparent total enthalpy change per mole of water, $\Delta H_1/n_0$, and of the apparent enthalpy change due to the dissolution of the hydrate solid per mole of water which forms hydrogen-bonded networks in the hydrate, $\Delta H_2/mn_1$, in the $(n\text{-}C_4H_9)_4$NPA–H_2O binary system. Dotted lines represent similar quantities for the $(n\text{-}C_4H_9)_4$NCl–H_2O system[15] for comparison.

$\Delta H_2/mn_1$, are plotted against the mole fraction X, together with the corresponding curves for the $(n\text{-}C_4H_9)_4$NCl–H_2O system.[15] The quantity $\Delta H_1/n_0$ means apparent, total enthalpy change per mole of water and the quantity $\Delta H_2/mn_1$ means apparent enthalpy change due to the dissolution of the hydrate solid per mole of water which forms hydrogen-bonded networks in the hydrate solid. These two quantities become equal at the congruent composition as expected from Eq. 1. Although these curves cannot be analyzed in detail because of the lack of other thermodynamic information (especially of the data concerning the enthalpies of mixing of a hydrate melt with water), a striking resemblance of these curves between the $(n\text{-}C_4H_9)_4$NPA hydrate and the $(n\text{-}C_4H_9)_4$NCl hydrate suggests that the thermal behavior of water molecules in the $(n\text{-}C_4H_9)_4$NPA hydrate is similar to that in the $(n\text{-}C_4H_9)_4$NCl hydrate. However, the value of $\Delta H_2/mn_1$ (or $\Delta H_1/n_0$) at the congruent composition for the $(n\text{-}C_4H_9)_4$NPA hydrate, 4.60 kJ mol^{-1}, is considerably smaller than that (5.47 kJ mol^{-1}) found for the $(n\text{-}C_4H_9)_4$NCl hydrate.[15] This suggests that the hydrogen-bonded water frameworks in the $(n\text{-}C_4H_9)_4$NPA hydrate are appreciably deformed as compared with those in the $(n\text{-}C_4H_9)_4$NCl hydrate.

Finally, the thermal behavior of the solutions whose X's are larger than 0.0330 must be briefly discussed. Only two solutions with X=0.0423 and X=0.0506 have been examined and the results are included in Table 2. The thermal behavior of the X=0.0423 solution is represented in Fig. 3. The heating curve indicates the existence of two kinds of hydrates. The hydrate which melts at a higher temperature is the same as that discussed above (m=30±1) judging from the value of the dissolution temperature as well as from the concentration dependence of ΔH_2. The hydration numbers, m', of the other hydrate can approximately be estimated by the following equation using m=30:

$$m' = \left(n_0 - \frac{\Delta H_2}{4.60\times 10^3}\right)\Bigg/\left(n_1 - \frac{\Delta H_2}{4.60\times 10^3 m}\right), \qquad (2)$$

where ΔH_2 is the second-step enthalpy change in the heating process, which is approximately separated from the total enthalpy change ΔH_1 (Table 2) and the value of 4.60×10^3 stands for the molar enthalpy of fusion (J unit) of the water which forms the hydrate of m=30 as determined above. The calculated values of m' are 16.8±1.9 for the X=0.0423 solution and 17.8±0.9 for the X=0.0506 solution, respectively. This hydrate seems to be a kind of clathrate-like hydrate since its melting point is high (about 6 °C) and its hydration number, m', is large (17—18) in comparison with that of ordinary hydrates of many other organic compounds.

(3) The Confirmation of the Formation of a Clathrate-Like Hydrate of Tetraisopentylammonium Polyacrylate. In a preliminary experiment it was found that when about 10 wt% aqueous solution of $(i\text{-}C_5H_{11})_4$NPA was cooled to about −20 °C, a transparent crystalline phase was obtained as well-formed prisms which remained undissolved even at 10 °C. This phenomenon suggests the formation of a solid phase other than ice. The cooling and heating curves for $(i\text{-}C_5H_{11})_4$NPA aqueous solutions are shown

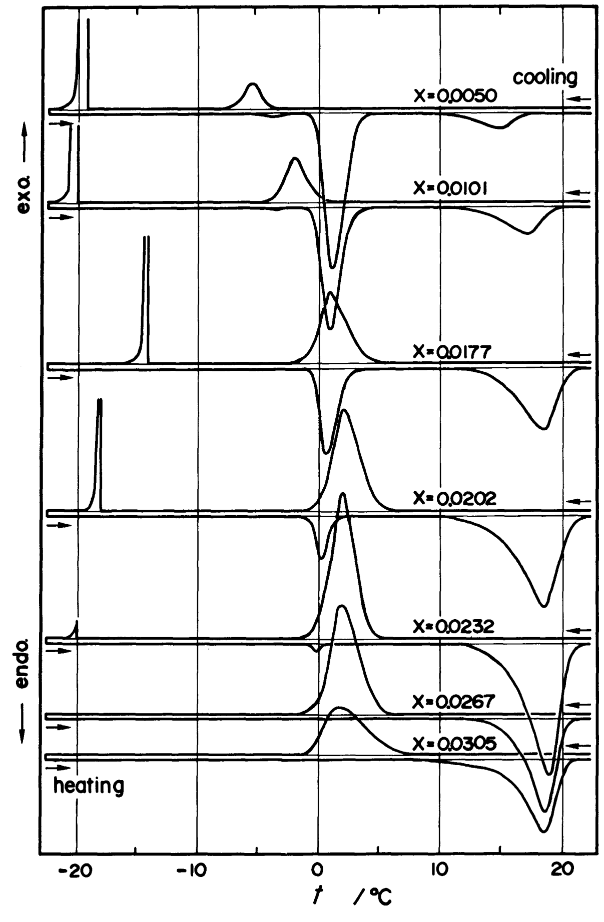

Fig. 7. Temperature dependence of the DSC signals, expressed in an arbitrary unit, for aqueous solutions of tetraisopenylammonium polyacrylate (($(i\text{-}C_5H_{11})_4NPA$) in various concentrations.

in Fig. 7 in a similar manner as in Fig. 3. The thermal behavior of these curves resembles that of the $(n\text{-}C_4H_9)_4NPA$ solutions, suggesting the formation of a clathrate-like hydrate of $(i\text{-}C_5H_{11})_4NPA$. Thus, these curves can be analyzed in the same way as those of the $(n\text{-}C_4H_9)_4NPA\text{-}H_2O$ system, giving each peak a similar physical meaning as before. Representative values of ΔH_1, ΔH_2, and dissolution temperatures observed, and the hydration numbers calculated by Eq. 1 are listed in Table 3.

The congruent composition, which gives the highest dissolution temperature (19.5 °C), is close to X=0.0232, indicating the hydration numbers of the $(i\text{-}C_5H_{11})_4NPA$ hydrate are around 42. The hydration numbers calculated for the solutions in the concentration range of X=0.0121—0.0232 are also around 42, although those for the solutions with X's smaller than 0.0121 are larger than 42. It is not clear whether another kind of hydrate which has larger hydration numbers than 42 is formed in such dilute solutions. In conclusion, $(i\text{-}C_5H_{11})_4NPA$ can form a clathrate-like hydrate with hydration numbers of 42±2 and melting point of 19.5 °C. The formation of such a hydrate has not been reported previously.

A solid-liquid phase diagram for the $(i\text{-}C_5H_{11})_4NPA\text{-}H_2O$ system, determined in the same manner as in the case of the $(n\text{-}C_4H_9)_4NPA\text{-}H_2O$ system, is also shown in Fig. 4, together with that of the $(i\text{-}C_5H_{11})_4NCl\text{-}H_2O$ system which has been known to form a clathrate-like hydrate with hydration numbers around 40.[7] The striking resemblance of the phase diagrams of both systems affords an additional reason for concluding that the $(i\text{-}C_5H_{11})_4NPA$ hydrate is a clathrate-like hydrate similar to the $(i\text{-}C_5H_{11})_4NCl$ hydrate whose crystal structure is believed to be iso-

Table 3. Dissolution Temperatures t, Enthalpy Changes ΔH_1 and ΔH_2, and Calculated Hydration Numbers m for Aqueous Solutions of Tetraisopentylammonium Polyacrylate

X	$\frac{n_0}{10^{-4}\text{mol}}$	$\frac{n_1}{10^{-5}\text{mol}}$	$\frac{t}{°\text{C}}$	$\frac{\Delta H_1{}^{a)}}{\text{J}}$	$\frac{\Delta H_2{}^{a)}}{\text{J}}$	m
0.0060	8.3967	0.5068	16.1	4.45±0.06	0.86±0.04	47.8±2.4
0.0080	7.8194	0.6312	17.0	4.07±0.07	1.07±0.06	44.8±2.4
0.0101	6.8868	0.6989	17.8	3.52±0.05	1.23±0.04	44.0±1.5
0.0121	8.2880	1.0116	18.4	4.27±0.06	1.81±0.04	41.5±1.2
0.0160	6.8302	1.1106	18.9	3.55±0.04	2.24±0.02	41.9±0.7
0.0202	7.7283	1.5928	19.3	4.02±0.05	3.37±0.03	41.7±0.6
0.0232	6.3787	1.5147	19.5	3.48±0.02	3.44±0.02	41.7±0.3
0.0244	5.8726	1.4691	19.4	3.18±0.03 (3.20)[b)]	3.18±0.03	—
0.0267	6.1725	1.6909	19.1	3.26±0.04 (3.36)[b)]	3.26±0.04	—
0.0305	5.1569	1.6205	18.9	2.45±0.03 (2.81)[b)]	2.45±0.03	—

All the notations are the same as those in Table 2.

a) These values are averages of 3—5 measurements. b) Calculated values from $5.45\times10^3 n_0$.

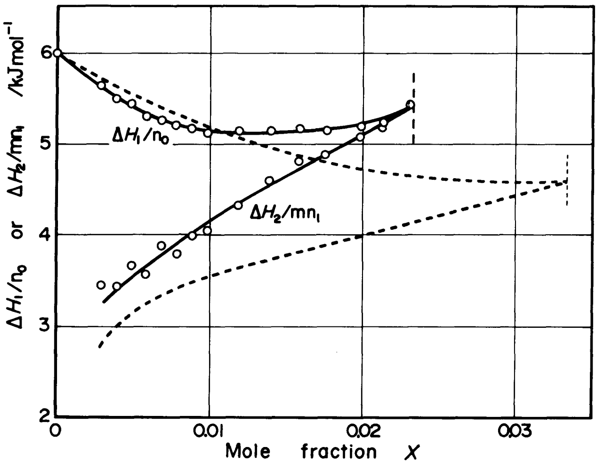

Fig. 8. The concentration dependence of $\Delta H_1/n_0$ and of $\Delta H_2/mn_1$ for the (i-$C_5H_{11})_4$NPA-H_2O system. The physical meaning of these quantities are identical with those in Fig. 6. Dotted lines represent similar quantities for the (n-$C_4H_9)_4$NPA-H_2O system (Fig. 6) for comparison.

structural with (i-$C_5H_{11})_4$NF hydrate.

According to the crystal structure examination of the (i-$C_5H_{11})_4$NF hydrate by Jeffrey et al.,[3] this hydrate consists of a regular arrangement of columns of tetrakaidecahedra extended in the c-axis direction by sharing hexagonal faces; these columns are connected by alternate layers of pentagonal dodecahedra and pentakaidecahedra which face-share congruently. A possible way to accommodate the polyacrylate chain in vacant pentagonal dodecahedra may be either to use the pentagonal dodecahedra layer extended in the direction perpendicular to the c-axis or to use pentagonal dodecahedra existing in the alternate layers in the c-axis direction by replacing fluorine atoms in the original (i-$C_5H_{11})_4$NF hydrate by oxygen atoms of carboxyl groups of the polyacrylate chain. Precise structural analysis is awaited. A single-crystal X-ray examination will be possible since the (i-$C_5H_{11})_4$NPA hydrate solid can be obtained as well-formed prisms.

In Fig. 8, the two apparent quantities, $\Delta H_1/n_0$ and $\Delta H_2/mn_1$, are plotted against the mole fraction X similarly to Fig. 6. The value of $\Delta H_2/mn_1$ (or of $\Delta H_1/n_0$) at the congruent composition is equal to 5.45 kJ mol^{-1}. This value is appreciably larger than that of the (n-$C_4H_9)_4$NPA hydrate (4.60 kJ mol^{-1}), indicating that the water networks in the (i-$C_5H_{11})_4$NPA hydrate are less deformed than those in the (n-$C_4H_9)_4$NPA hydrate. This results coincides with a general trend that the water frameworks surrounding a (i-$C_5H_{11})_4N^+$ cation are more stable than those surrounding a (n-$C_4H_9)_4N^+$ cation if both cations have the same kind of anions.[17]

The thermal behavior of the solutions with X's higher than the congruent composition (X=0.0267 and 0.0305 in Fig. 7 and X=0.0244, 0.0267, and 0.0305 in Table 3) shows no formation of another kind of hydrate other than the one discussed above (m=42±2). In Table 3 the observed values of ΔH_1 (or of ΔH_2) are compared with the values calculated by a relation of $5.45\times10^3 n_0$. The quantity, $5.45\times10^3 n_0$, means the enthalpy of fusion of the hydrate (J unit) if we assume that all the water molecules participate in the hydrate formation and further that the enthalpy of fusion is equal to 5.45 kJ mol^{-1} as determined above. The observed value of ΔH_1 for X=0.0244 solution is almost compatible with the calculated one, whereas in more concentrated solutions (X=0.0267 and 0.0305) the observed values of ΔH_1 become small as compared with the calculated ones. At present a quantitative interpretation cannot be made because of a lack of information concerning the state of the solid-liquid mixture in such concentrated solutions.

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References

1) R. K. McMullan, M. Bonamico, and G. A. Jeffrey, *J. Chem. Phys.*, **39**, 3295 (1963).
2) M. Bonamico, G. A. Jeffrey, and R. K. McMullan, *J. Chem. Phys.*, **37**, 2219 (1962).
3) D. Feil and G. A. Jeffrey, *J. Chem. Phys.*, **35**, 1863 (1961).
4) 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).
5) R. McMullan and G. A. Jeffrey, *J. Chem. Phys.*, **31**, 1231 (1959).
6) H. Nakayama and K. Watanabe, *Bull. Chem. Soc. Jpn.*, **49**, 1254 (1976).
7) H. Nakayama, *Bull. Chem. Soc. Jpn.*, **54**, 3717 (1981).
8) G. Beurskens, G. A. Jeffrey, and R. K. McMullan, *J. Chem. Phys.*, **39**, 3311 (1963).
9) H. Nakayama and K. Watanabe, *Bull. Chem. Soc. Jpn.*, **51**, 2518 (1978).
10) H. Nakayama and S. Torigata, *Bull. Chem. Soc. Jpn.*, **57**, 171 (1984).
11) H. Nakayama and H. Usui, *J. Inclusion Phenomena*, **2**, 249 (1984).
12) Yu. A. Dyadin, L. S. Aladko, L. A. Gaponenko, and T. M. Polyanskaya, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, **1981**, 19.
13) A. Takahashi, Y. Hayashi, and I. Kagawa, *Kogyo Kagaku Zasshi*, **60**, 113 (1957).
14) D. Eisenberg and W. Kauzmann, "The Structure and Properties of Water," Oxford Univ. Press, London (1969).
15) H. Nakayama, *Bull. Chem. Soc. Jpn.*, **60**, 839 (1987).
16) H. Nakayama, *Bull. Chem. Soc. Jpn.*, **56**, 877 (1983).
17) H. Nakayama, *Bull. Chem. Soc. Jpn.*, **55**, 389 (1982).