# The effect of simple anions on the formation of poly(tetraisopentylammonium acrylate) hydrates

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## Abstract

In order to know the effect of simple anions on the formation of a poly(tetraisopentyl-ammonium acrylate) ((i-$C_5H_{11}$)$_4$NPA) hydrate, a thermal analytic method using a differential scanning calorimeter was applied to (a) aqueous solutions of (i-$C_5H_{11}$)$_4$NPA whose PA anion is partially replaced with simple anions like Cl$^-$ and $C_2H_5COO^-$, (i-$C_5H_{11}$)$_4$N[PA]$_{1-x}$Cl$_x$ and (i-$C_5H_{11}$)$_4$N[PA]$_{1-x}$[$C_2H_5COO$]$_x$ ($x = 0$–$1.0$), and to (b) aqueous solutions of (i-$C_5H_{11}$)$_4$NPA containing either NaCl or $C_2H_5COONa$. It was found that when Cl$^-$ ion coexisted with the PA anion, two kinds of hydrates, i.e. (i-$C_5H_{11}$)$_4$NPA hydrate and (i-$C_5H_{11}$)$_4$NCl hydrate, were formed separately, and a solid solution phase containing both (i-$C_5H_{11}$)$_4$NPA hydrate and (i-$C_5H_{11}$)$_4$NCl hydrate was not detected. In addition, in the (i-$C_5H_{11}$)$_4$NPA + NaCl systems, the amount of (i-$C_5H_{11}$)$_4$NCl hydrate increased and the PA anion was gradually expelled from the hydrate phase on increasing the amount of NaCl. The behavior of the $C_2H_5COO^-$ ion was almost the same as that of the Cl$^-$ ion.

*Keywords:* Ammonium compound; Anion; DSC; Halide; Hydrate

## 1. Introduction

Several years ago, one of the authors first found that both poly(tetrabutylammonium acrylate) and poly(tetraisopentylammonium acrylate) could form characteristic hydrates having fairly high melting points (11.2 and 19.5°C) and large hydration

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numbers (30 and 42) [1]. From the melting points, hydration numbers, and the concentration dependence of the dissolution temperatures, it was concluded that these hydrates were clathrate-like hydrates similar to those formed by various tetrabutylammonium salts and tetraisopentylammonium salts such as $(n\text{-}C_4H_9)_4NF$ [2] and $(i\text{-}C_5H_{11})_4NF$ [3]. The fairly high stability (high melting point) of these hydrates is due to the fact that hydrogen-bonded water networks (host structure) around either the tetrabutylammonium or tetraisopentylammonium cation can be constructed so stably that their stabilities overcome the unfavorable condition that a long polyacrylate chain must be regularly accommodated within the hydrate crystal.

In this study, in order to know the effect of a polyacrylate anion on the stability of a hydrate and the difference in the behavior of anions between polyacrylate anion and a simple anion such as $Cl^-$ and $C_2H_5COO^-$, two types of poly(tetraisopentyl-ammonium acrylate) solutions were examined by a thermal analytic method using a differential scanning calorimeter (DSC), namely aqueous solutions of poly(tetra-isopentylammonium acrylate) in which the polyacrylate anion is partially replaced with another simple anion like $Cl^-$ and $C_2H_5COO^-$, $(i\text{-}C_5H_{11})_4N[PA]_{1-x}Cl_x$ and $(i\text{-}C_5H_{11})_4N[PA]_{1-x}[C_2H_5COO]_x$ $(x = 0\text{-}1.0)$, in which PA denotes one unit of the polyacrylate anion, and aqueous solutions of poly(tetraisopentylammonium acry-late) with added salt such as NaCl and $C_2H_5COONa$, $(i\text{-}C_5H_{11})_4NPA + y\,NaCl$ and $(i\text{-}C_5H_{11})_4NPA + y\,C_2H_5COONa$ $(y = 0\text{-}1.2)$. $C_2H_5COO^-$ ion was used as one of the simple anions because it has a chemical structure similar to that of the PA anion, $-CH_2CH(COO^-)-$. Furthermore, prior to the investigation of the solution men-tioned above, related systems containing low-molecular-weight anions only, i.e. $(n\text{-}C_4H_9)_4NCl_{1-x}F_x$ and $(n\text{-}C_4H_9)_4NCl + y\,KF$, were also examined by the same thermal analytic method in order to determine the difference in the behaviors between PA anion and simple $Cl^-$ ion.

## 2. Experimental

An aqueous solution of poly(tetraisopentylammonium acrylate) was obtained by the neutralization of an aqueous solution of poly(acrylic acid) with an aqueous solution of tetraisopentylammonium hydroxide $(i\text{-}C_5H_{11})_4NOH$. The aqueous solu-tion of $(i\text{-}C_5H_{11})_4NOH$ was prepared by reacting tetraisopentylammonium iodide, $(i\text{-}C_5H_{11})_4NI$, with freshly prepared silver(I) oxide in water with vigorous stirring, followed by filtration of the resulting silver iodide in a $CO_2$-free atmosphere. The $(i\text{-}C_5H_{11})_4NI$ was synthesized and purified by the same procedure as reported earlier [4]. An aqueous solution of poly(acrylic acid) was purchased from Wako Pure Chemical Industries, Ltd. and was used without further purification. The mean degree of polymerization of poly(acrylic acid) was estimated to be about 2100 from viscosity measurements of aqueous solutions of its sodium salt in 1 mol dm$^{-3}$ NaCl solution at 25°C using the equation proposed by Takahashi et al. [5]. The aqueous solutions $(i\text{-}C_5H_{11})_4N[PA]_{1-x}Cl_x$ and $(i\text{-}C_5H_{11})_4N[PA]_{1-x}[C_2H_5COO]_x$ $(x = 0\text{-}1.0)$ were obtained by neutralization of an aqueous solution of (i-

$C_5H_{11})_4NOH$ with a mixture of two acids, either poly(acrylic acid) plus hydrochloric acid or poly(acrylic acid) plus propionic acid, with definite values of $x$.

The differential scanning calorimeter used was a model DSC10 with an SSC580 thermal controller manufactured by Seiko Instruments and Electronics Ltd. Sample solutions (about 15 mg) of known concentrations were sealed in a 15 $\mu$l aluminium pan. The DSC signal was measured by either cooling or heating at a rate of 0.5°C min$^{-1}$. An empty 15 $\mu$l aluminium pan was used as a reference.

## 3. Results and discussion

### 3.1. The effect of fluoride ions on the formation of (n-$C_4H_9)_4$NCl hydrates

In order to know the effect of coexisting simple anions on the formation of a hydrate, the behavior of aqueous solutions of $(n\text{-}C_4H_9)_4NCl$ in the presence of $F^-$ ion was examined. As an ammonium cation, $(n\text{-}C_4H_9)_4N^+$ ion was used instead of $(i\text{-}C_5H_{11})_4N^+$ ion because the melting points of the two hydrates, $(i\text{-}C_5H_{11})_4NCl$ hydrate and $(i\text{-}C_5H_{11})_4NF$ hydrate, are so close to each other (29.6 and 31.5°C [6]) that separation of the DSC signals corresponding to each hydrate is difficult.

Fig. 1 shows the cooling and heating DSC for aqueous solutions of tetrabutylammonium chloride whose anion is substituted successively by fluoride ion, $(n\text{-}C_4H_9)_4NCl_{1-x}F_x$ ($x = 0$–1.0), as a function of $x$. The mole fractions of all the solutions are equal to 0.02. It is obvious that both the exothermic peaks around $-20$°C and the endothermic peaks around 0°C indicate the solidification of a supercooled water upon cooling and the melting of ice upon heating, respectively. Therefore, both the exothermic peaks around $-10$ to 0°C and the endothermic peaks around 10–30°C are obviously correlated to the solidification and melting of a hydrate phase. The dissolution temperature of a hydrate upon heating increases with increasing $x$. It is interesting to note that in the solutions of $x = 0.1$–0.9 (some of which are omitted from Fig. 1 for simplicity) there is only one exothermic peak and only one endothermic peak associated with the hydrate phase. This indicates that $(n\text{-}C_4H_9)_4NCl_{1-x}F_x$ hydrate is a uniform hydrate, like a solid solution with $(1 - x)(n\text{-}C_4H_9)_4NCl$ hydrate and $x(n\text{-}C_4H_9)_4NF$ hydrate, not a hetrogeneous mixture of the $(n\text{-}C_4H_9)_4NCl$ hydrate phase and $(n\text{-}C_4H_9)_4NF$ hydrate phase. In this hydrate crystal, two kinds of anions, $Cl^-$ and $F^-$, seem to be uniformly distributed according to the value of $x$. The possibility of the formation of a solid-solution-type hydrate may be because $(n\text{-}C_4H_9)_4NCl$ hydrate and $(n\text{-}C_4H_9)_4NF$ hydrate have same hydration numbers [4], around 30, and because they are isomorphous crystals with the same unit cell dimensions [7]. A solid–liquid phase diagram of an $(n\text{-}C_4H_9)_4NCl \cdot 30H_2O + (n\text{-}C_4H_9)_4NF \cdot 30H_2O$ system also supports this conclusion [8]. The results shown in Fig. 1 also indicate that both the melting points and enthalpies of fusion of the $(n\text{-}C_4H_9)_4NCl_{1-x}F_x$ hydrate increase almost linearly with increasing $x$: from 15.0°C and 155 kJ mol$^{-1}$ when $x = 0$, to 28.5°C and 185 kJ mol$^{-1}$ when $x = 1.0$.

Fig. 2 shows some representative DSC signals for aqueous solutions of $(n\text{-}C_4H_9)_4NCl$ with added KF. The value $y$ indicates the molar ratio of KF to
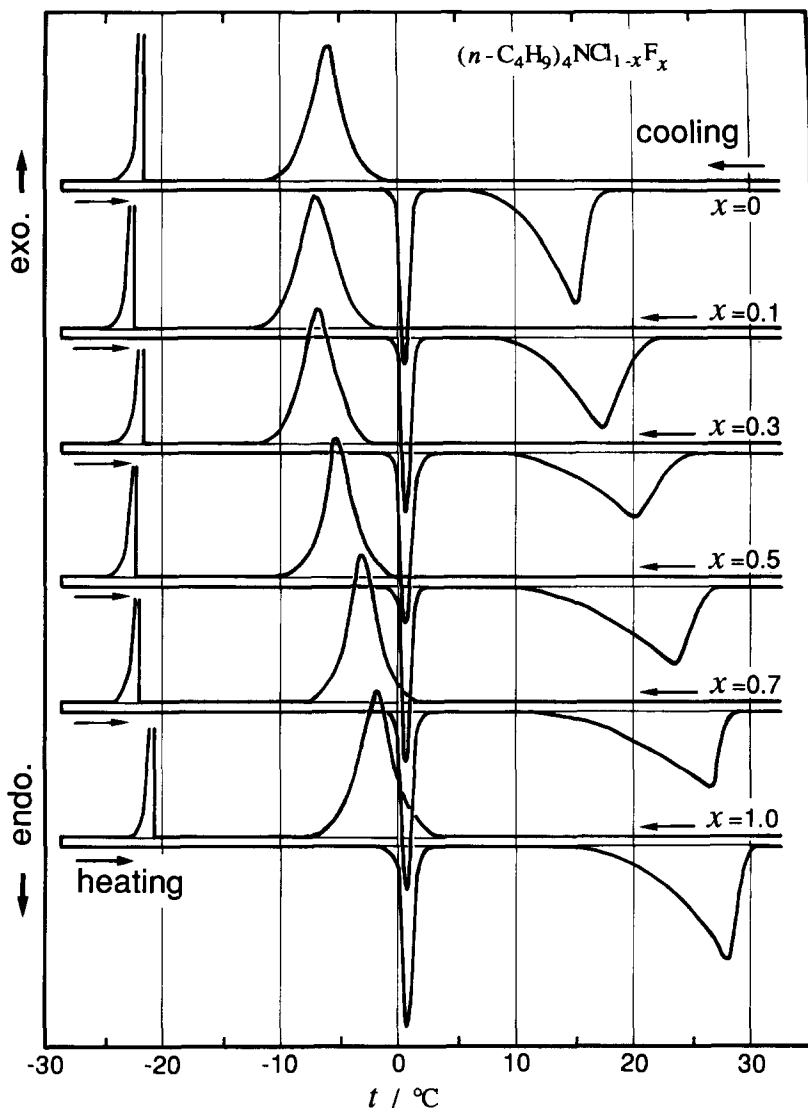
Fig. 1. Temperature dependence of the DSC signals, expressed in an arbitrary unit, for aqueous solutions of $(n\text{-}C_4H_9)_4NCl_{1-x}F_x$ $(x = 0\text{--}1.0)$.

$(n\text{-}C_4H_9)_4NCl$. The ratio of the number of moles of water to that of $(n\text{-}C_4H_9)_4NCl$ is the same as in Fig. 1, i.e. 49. Fig. 2 clearly shows that the thermal behavior of the hydrate phase is essentially the same as in the one shown in Fig. 1 except that the dissolution temperatures of the hydrate are slightly low when two solutions with the same values of $y$ and $x$ are compared. This may be due to the melting point depression of the hydrate phase by the addition of KF. Fig. 2 also shows that the endothermic peak of the ice phase is affected by the addition of KF and the
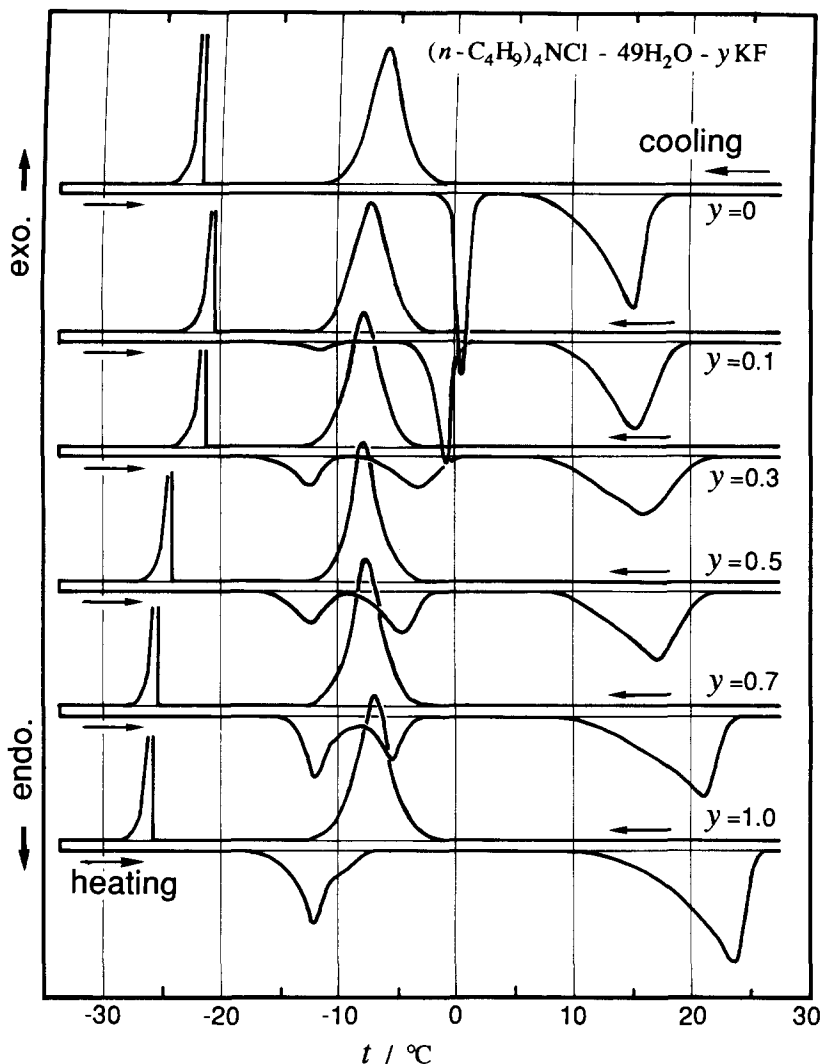
Fig. 2. Temperature dependence of the DSC signals, expressed in an arbitrary unit, for the systems $(n\text{-}C_4H_9)_4NCl\text{–}49H_2O\text{–}yKF$ ($y = 0\text{–}1.0$).

appearance of another endothermic peak at around $-12°C$ may be due to the eutectic behavior between water and KF under the influence of the tetrabutylam-monium salt.

A similar thermal behavior of the hydrate phase to that shown in Fig. 1 indicates the formation of a homogeneous hydrate which contains both $Cl^-$ ion and $F^-$ ion in solutions with $y$ greater than 0, suggesting that the $(n\text{-}C_4H_9)_4N^+$ cation gathers as many $F^-$ ions as possible and forms a more stable hydrate than $(n\text{-}C_4H_9)_4NCl$ hydrate. The incorporation of $F^-$ ion into a hydrate phase seems to be completed

when $y = 1.0$, because DSC signals of the hydrate phase in solutions of $y = 1.2$, omitted from Fig. 2 for simplicity, are almost the same as those in the case of $y = 1.0$. The hydrate phase formed in the solutions of $y$ either equal to or greater than 1 is the $(n\text{-}C_4H_9)_4NF$ hydrate.

## 3.2. Effect of chloride ions on the formation of $(i\text{-}C_5H_{11})_4NPA$ hydrate

The cooling and heating curves in the DSC measurements for aqueous solutions of poly(tetraisopentylammonium acrylate) whose polyacrylate anion, PA, is substituted successively by chloride ion, $(i\text{-}C_5H_{11})_4N[PA]_{1-x}Cl_x$ ($x = 0$–$1.0$), are shown in Fig. 3 as a function of $x$. The mole fractions of all the solutions are equal to 0.02. Both the exothermic peaks around $-15°C$ and the endothermic peaks around $0°C$ indicate the solidification of supercooled water and the melting of ice, as in Figs. 1 and 2. However, the amounts of heat either evolved or absorbed are relatively small as compared with those shown in Figs. 1 and 2 as a result of the decrease in the amount of free water because a tetraisopentylammonium salt forms a hydrate with a hydration number of about 40 [2,4,6] instead of about 30 for a tetrabutylammonium salt hydrate.

Other exothermic peaks at around $0$–$10°C$ and endothermic peaks at around $10$–$30°C$ clearly indicate the solidification and melting of a hydrate phase. It is interesting to note that, except for the solution of $x = 0$ (($i\text{-}C_5H_{11})_4NPA$) and $x = 1.0$ (($i\text{-}C_5H_{11})_4NCl$), two endothermic peaks corresponding to the melting of hydrate phase can be found, although there is a single exothermic peak on cooling. This clearly indicates that in these solutions two kinds of hydrates are formed and, further, that the one having an endothermic peak at around $15°C$ is an ($i$-$C_5H_{11})_4NPA$ hydrate and the other near $30°C$ is the more stable ($i\text{-}C_5H_{11})_4NCl$ hydrate. The former hydrates are even formed in solutions with $x = 0.9$ and the latter, even with $x = 0.1$. The probable reason for only one exothermic peak on cooling may be explained by considering that the formation of these two kinds of hydrates from a supercooled solution occurs simultaneously. The formation of two kinds of hydrates in the solutions containing both polyacrylate anion and chloride ion is a striking difference as compared with the formation of one kind of homogeneous hydrate in the solutions containing two simple anions, $F^-$ and $Cl^-$, as shown in Fig. 1. Although the reason for the coexistence of two kinds of hydrates, ($i\text{-}C_5H_{11})_4NPA$ hydrate and ($i\text{-}C_5H_{11})_4NCl$ hydrate, is not clear at present, it seems to be owing to the situation that a long polyacrylate anion cannot easily be replaced with a large number of $Cl^-$ ions in a solid hydrate.

The DSC signals of the solutions of poly(tetraisopentylammonium acrylate) with added NaCl, ($i\text{-}C_5H_{11})_4NPA + y\,NaCl$, are shown in Fig. 4 as a function of $y$. The value of $y$ indicates the molar ratio of added NaCl to the ($i\text{-}C_5H_{11})_4NPA$, as in Fig. 2. The number of moles of water is 49 times that of the ($i\text{-}C_5H_{11})_4NPA$ in all the solutions. Fig. 4 clearly shows that the thermal behavior of the hydrate phase is essentially the same as that shown in Fig. 3, indicating that: two kinds of hydrates, ($i\text{-}C_5H_{11})_4NPA$ hydrate and ($i\text{-}C_5H_{11})_4NCl$ hydrate, coexist; the amount of the former hydrate decreases and the latter increases with increasing value of $y$; and the
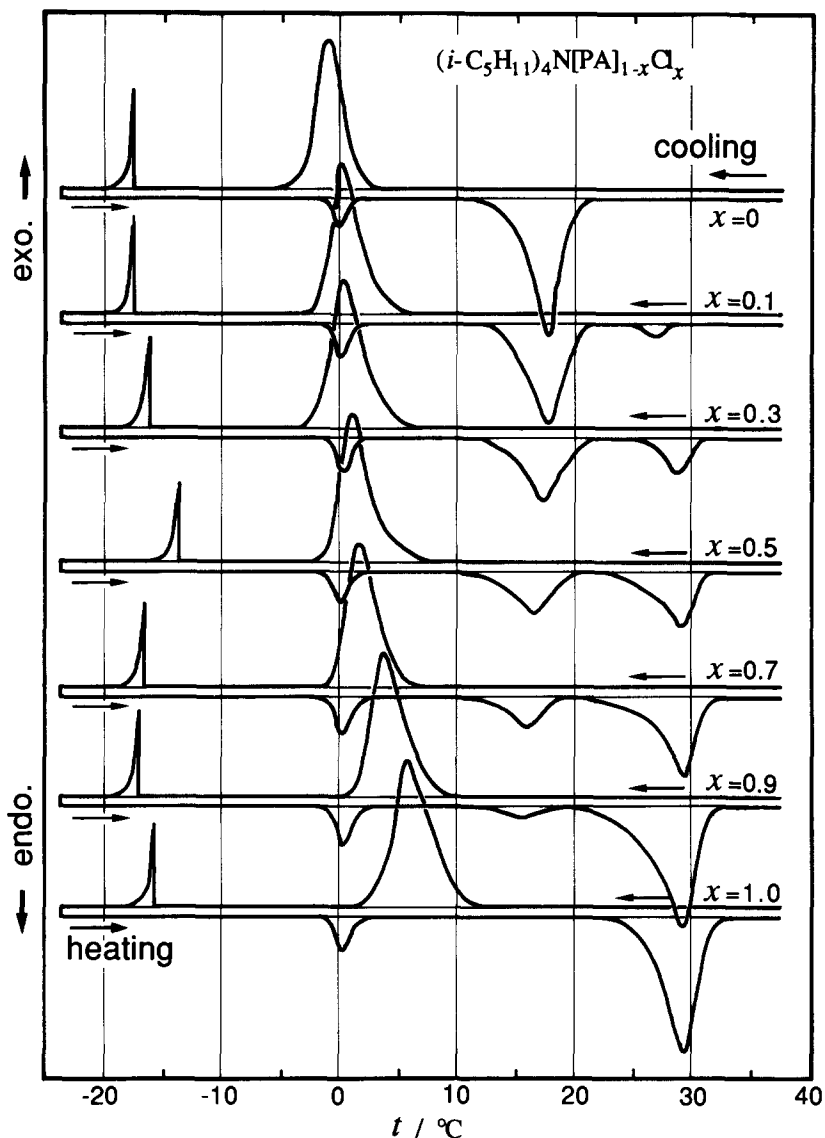
Fig. 3. Temperature dependence of the DSC signals, expressed in an arbitrary unit, for aqueous solutions of $(i\text{-}C_5H_{11})_4N[PA]_{1-x}Cl_x$ ($x = 0$–$1.0$). PA denotes one unit of the polyacrylate anion.

$(i\text{-}C_5H_{11})_4NPA$ hydrate disappears in the solution of $y = 1.0$, although in principle its formation is possible unlike the case shown in Fig. 3. The disappearance of the $(i\text{-}C_5H_{11})_4NPA$ hydrate in the solution of $y = 1.0$ (and $y = 1.2$) is attributable to the situation that the $(i\text{-}C_5H_{11})_4N^+$ ion gathers as many $Cl^-$ ions as possible and forms more stable $(i\text{-}C_5H_{11})_4NCl$ hydrate rather than $(i\text{-}C_5H_{11})_4NPA$ hydrate, as
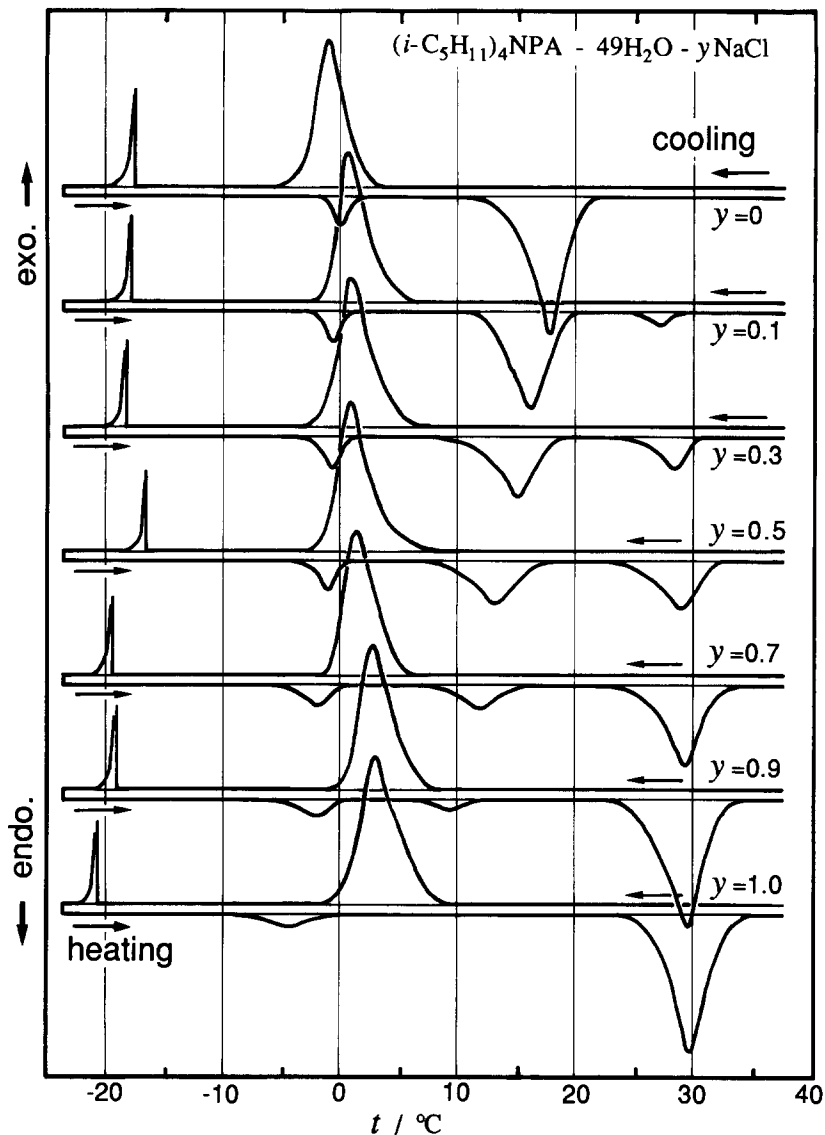
Fig. 4. Temperature dependence of the DSC signals, expressed in an arbitrary unit, for the systems $(i-C_5H_{11})_4NPA-49H_2O-yNaCl$ ($y = 0-1.0$). PA denotes one unit of the polyacrylate anion.

demonstrated with respect to the solution with $y = 1.0$ in Fig. 2. The dissolution temperatures of the polyacrylate hydrate decrease more markedly with increasing $y$ as compared with the results shown in Fig. 3. This may be attributable either to the formation of unstable hydrate such as $[(i-C_5H_{11})_4N]_z Na_{1-z} PA$ hydrate or, simply, to a gradual increase in the amount of NaPA in the solutions.

### 3.3. Effect of propionate ions on the formation of (i-C₅H₁₁)₄NPA hydrates

The DSC signals of aqueous solutions of $(i\text{-}C_5H_{11})_4N[PA]_{1-x}[C_2H_5COO]_x$ $(x = 0-1.0)$ and of $(i\text{-}C_5H_{11})_4NPA$ with added $C_2H_5COONa$ are shown in Figs. 5 and 6, respectively. It is clear that the results shown in Fig. 5 very much resemble those shown in Fig. 3 and similarly those shown in Fig. 6 resemble those in Fig. 4.
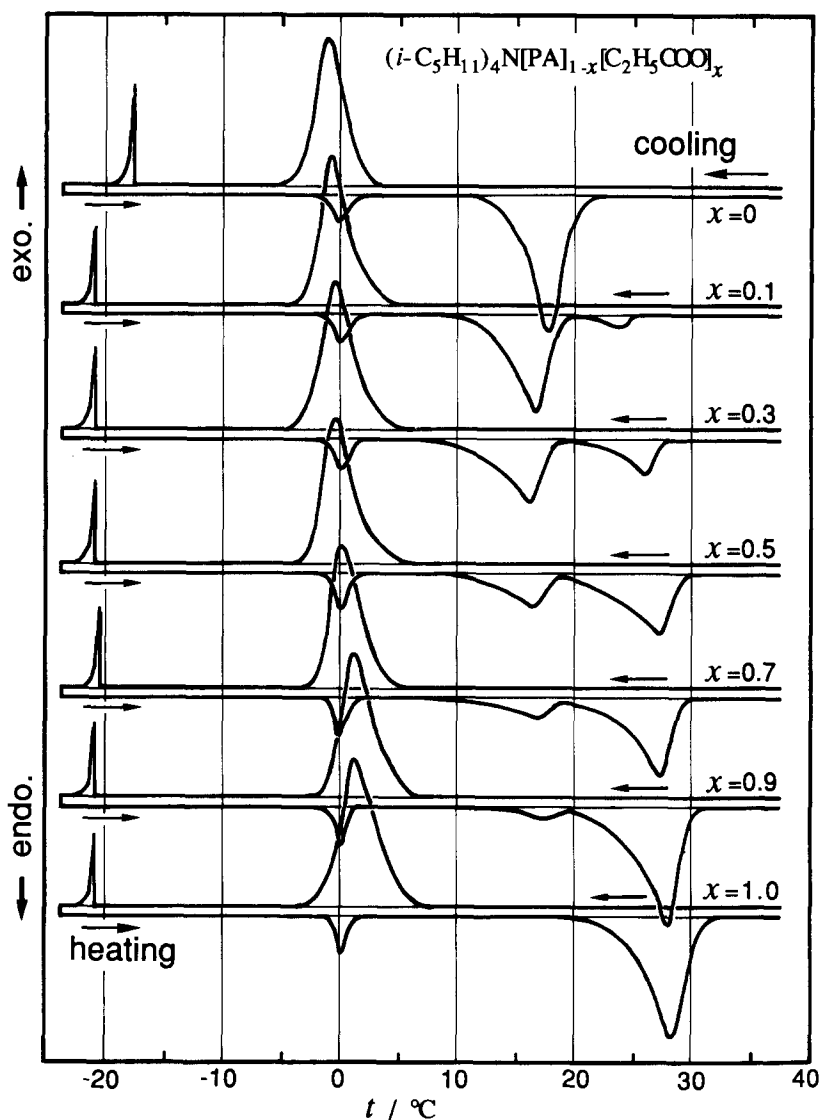


Fig. 5. Temperature dependence of the DSC signals, expressed in an arbitrary unit, for aqueous solutions of $(i\text{-}C_5H_{11})_4N[PA]_{1-x}[C_2H_5COO]_x$ $(x = 0-1.0)$. PA denotes one unit of the polyacrylate anion.
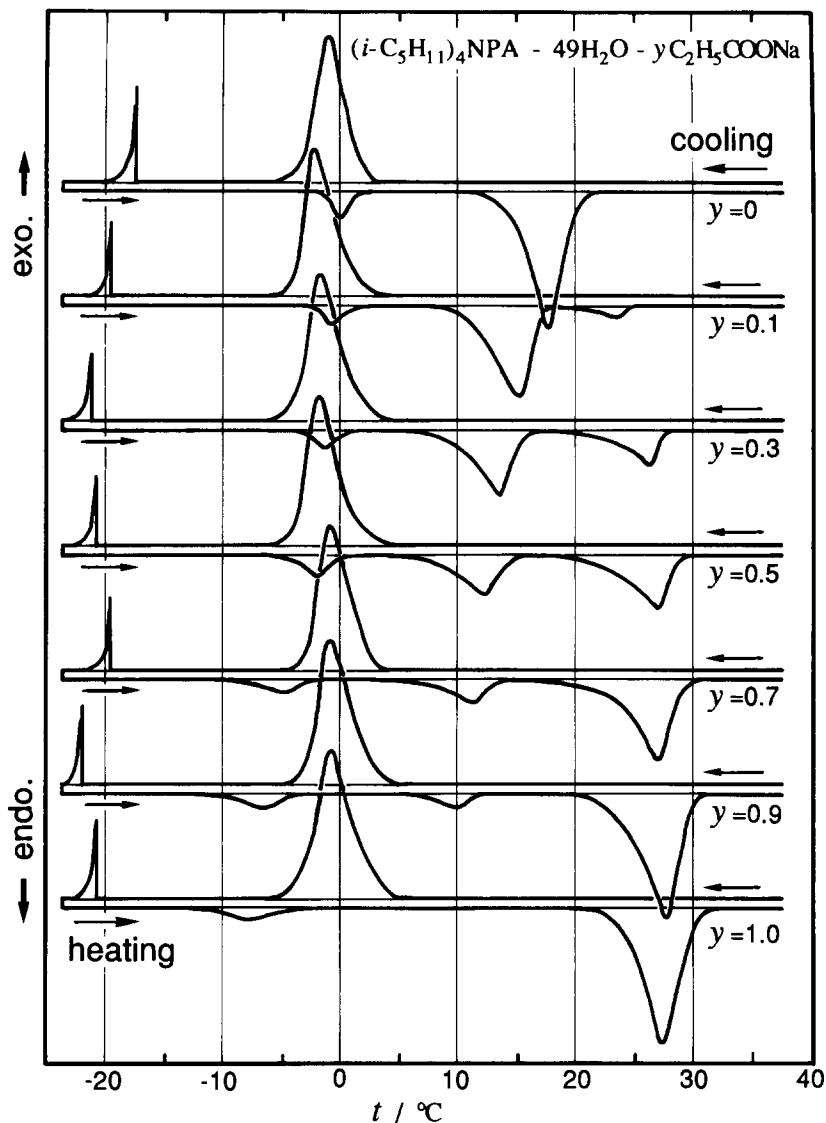
Fig. 6. Temperature dependence of the DSC signals, expressed in an arbitrary unit, for the systems $(i\text{-}C_5H_{11})_4NPA\text{-}49H_2O\text{-}yC_2H_5COONa$ ($y = 0\text{-}1.0$). PA denotes one unit of the polyacrylate anion.

The hydrate having the highest melting point is a $(i\text{-}C_5H_{11})_4NC_5H_5COO$ hydrate [9] rather than the $(i\text{-}C_5H_{11})_4NCl$ hydrate in Figs. 3 and 4. Thus, following the same arguments mentioned above, we may arrive at the conclusion that a mixture of $(i\text{-}C_5H_{11})_4NPA$ hydrate and $(i\text{-}C_5H_{11})_4NC_2H_5COO$ hydrate exists. It is interesting to note that the $(i\text{-}C_5H_{11})_4NPA$ salt cannot form a homogeneous hydrate with $(i\text{-}C_5H_{11})_4NC_2H_5COO$ hydrate, in spite of the fact that the chemical structure of the $C_2H_5COO^-$ ion is very similar to that of the PA ion. Furthermore, distinction

between the $Cl^-$ ion and $C_2H_5COO^-$ ion with respect to the state within a hydrate crystal has no effect on the behavior of the $(i\text{-}C_5H_{11})_4NPA$ hydrate. In a hydrate crystal, $Cl^-$ ion and oxygen atoms of the $C_2H_5COO^-$ ion are hydrogen-bonded to the water framework and form part of the polyhedral structure; however, the $C_2H_5$ group of the $C_2H_5COO^-$ ion is located in the cavities of a hydrogen-bonded clathrate framework [9,10].

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