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Hydrates of Organic Compounds. XVII.
The Effect of Cations on the Formation of Hydrates of Poly(tetraisopentylammonium acrylate)

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A thermal analytic method using a differential scanning calorimeter was applied to binary mixtures of water with a series of poly(tetraisopentylammonium acrylates) whose cation was partially substituted by such cations as Na^+, $(n\text{-}C_3H_7)_4N^+$, and $(n\text{-}C_4H_9)_4N^+$ ($C_x[(i\text{-}C_5H_{11})_4N]_{1-x}PA$; C=Na, $(n\text{-}C_3H_7)_4N$, and $(n\text{-}C_4H_9)_4N$; x=0.1—0.9; PA=one unit of a polyacrylate anion). It was found that (1) when C=Na, the formation of a hydrate solid is possible, even in a system of x=0.9, though both the dissolution temperatures and the amounts of heat absorbed to melt the hydrate solid decreased with increasing x; (2) the effect of the $(n\text{-}C_3H_7)_4N^+$ ion was essentially similar to that of the Na^+ ion, except that the temperature at which the ice phase began to melt decreased pronouncedly with increasing x; and (3) in the case of the $[(n\text{-}C_4H_9)_4N]_x[(i\text{-}C_5H_{11})_4N]_{1-x}PA$ system it was concluded that the solid phase was essentially a $(i\text{-}C_5H_{11})_4NPA$ hydrate when x was smaller than about 0.4, a $(n\text{-}C_4H_9)_4NPA$ hydrate when x was larger than about 0.7 and some intermediate hydrate phase when x was around 0.5.

In a recent paper[1] we first reported 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 a large number of water molecules (30 and 42) per one unit of the polyacrylate anion (hydration numbers). It was concluded that these hydrates were clathrate-like hydrates similar to those formed by various types of tetrabutylammonium salts[2—4] and tetraisopentylammonium salts.[5—7] From the experimental results concerning such types of hydrates, it has been clarified that the most important factor which makes possible the formation of these hydrates is the fact that a stable cage-like structure of hydrogen-bonded water molecules can be constructed around a tetrabutylammonium ion and a tetraisopentylammonium ion.

In this study, in order to determine the effect of a cation on the stability of a poly(tetraisopentylammonium acrylate) hydrate, the behavior of aqueous solutions of polyacrylates in which the tetraisopentylammonium cation is partially replaced with another cation C, $C_x[(i\text{-}C_5H_{11})_4N]_{1-x}PA$ (x=0.1—0.9; PA denotes one unit of polyacrylate anion), was examined by a thermal analytic method using a differential scanning calorimeter. As a cation (C), three kinds of cations, Na^+, $(n\text{-}C_3H_7)_4N^+$, and $(n\text{-}C_4H_9)_4N^+$ were chosen for the following reasons: Sodium ion was chosen as an example of a simple inorganic cation whose polyacrylate, itself (NaPA), cannot form any hydrate;[1] the $(n\text{-}C_3H_7)_4N^+$ cation was chosen as an ammonium cation around which the construction of hydrogen-bonded water networks may be expected to a certain extent, even though $(n\text{-}C_3H_7)_4NPA$, itself, cannot form a stable hydrate;[1] and the $(n\text{-}C_4H_9)_4N^+$ cation was used as an ammonium cation whose polyacrylate can form a clathrate-like hydrate, but having different hydration numbers, about 30, from that of the $(i\text{-}C_5H_{11})_4NPA$ hydrate, about 42:[1] Both hydrates seem to have different crystal structures judging from the different hydration numbers. It would be interesting to know how the structure of the $(i\text{-}C_5H_{11})_4NPA$ hydrate is converted into that of the $(n\text{-}C_4H_9)_4NPA$ hydrate with increasing x.

Experimental

Aqueous solutions of poly(tetraisopentylammonium acrylates), $(i\text{-}C_5H_{11})_4NPA$, were obtained by neutralizing an aqueous solution of poly(acrylic acid) with an aqueous solution of tetraisopentylammonium hydroxide. The 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 the aqueous solutions of its sodium salt in a 1 mol dm^{-3} NaCl solution at 25 °C using an equation proposed by Kagawa et al.[8] Aqueous solutions of tetraisopentylammonium hydroxide were prepared by reacting tetraisopentylammonium iodide with freshly prepared silver(I) oxide in water with vigorous shaking, followed by filtration of the resulting silver iodide in a CO_2-free atmosphere. The tetraisopentylammonium iodide was synthesized by reacting triisopentylamine with isopentyl iodide in ethyl acetate, and was subsequently purified by repeated recrystallization from an ethyl acetate–acetone mixture.[9] Both triisopentylamine and isopentyl iodide were purchased from the Tokyo Kasei Kogyo Co. Aqueous solutions of $C_x[(i\text{-}C_5H_{11})_4N]_{1-x}PA$ (C=Na, $(n\text{-}C_3H_7)_4N$, and $(n\text{-}C_4H_9)_4N$) were prepared by neutralization of the poly(acrylic acid) solution with aqueous solutions of both tetraisopentylammonium hydroxide and one of the hydroxide COH (NaOH, $(n\text{-}C_3H_7)_4NOH$, and $(n\text{-}C_4H_9)_4NOH$) solutions. The hydroxide solutions, $(n\text{-}C_3H_7)_4NOH$ and $(n\text{-}C_4H_9)_4NOH$, were obtained in a similar way as the $(i\text{-}C_5H_{11})_4NOH$ solution mentioned above. The concentration of each mother solution was determined by measuring the amount of tetraisopentylammonium cation by titration with a sodium tetraphenylborate solution standardized by pure tetrabutylammonium iodide.

The differential scanning calorimeter used was model DSC-

10 with a 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 a rate of 0.5 °C per minute. An empty 15 µl aluminum pan was used as a reference.

Results and Discussion

(1) Formation of Hydrate in the $Na_x[(i\text{-}C_5H_{11})_4N]_{1-x}$ PA-H_2O Systems. In Fig. 1 the cooling and heating curves in differential scanning calorimetry (DSC) for aqueous solutions of a series of poly(tetraisopentylammonium acrylates) whose cation is partly substituted by sodium ion, $Na_x[(i\text{-}C_5H_{11})_4N]_{1-x}PA$ (x=0—1.0), are shown as a function of x. The results for systems with x=0.2 and 0.4 were eliminated in order to avoid complexity. The mole fractions (based on the monomeric unit of the polyacrylate ion) of all the solutions are equal to 0.02. The uppermost curve for the x=0 system, i.e., the $(i\text{-}C_5H_{11})_4NPA\text{-}H_2O$ system, is just the same as that reported in a previous paper.[1] Both the exothermic peak **A** on cooling and the endothermic peak **D** on heating clearly indicate the formation of a solid phase other than ice. It was concluded that this solid phase was a hydrate whose congruent melting point and hydration numbers are 19.5 °C and about 42, respectively.[1] As can be seen in Fig. 1 both the solidification temperature of a supercooled hydrate upon cooling and the dissolution temperature of a hydrate upon heating decrease with increasing x. The amounts of heat evolved in peak **A** and absorbed in peak **D** also decrease with increasing x. These results clearly indicate that the stability of the hydrogen-bonded water networks around the $(i\text{-}C_5H_{11})_4N^+$ cation gradually decreases with increasing the amount of Na^+ ion. However, it is very interesting to note that the heat change due to melting the hydrate phase can be observed even in a solution with x=0.9.

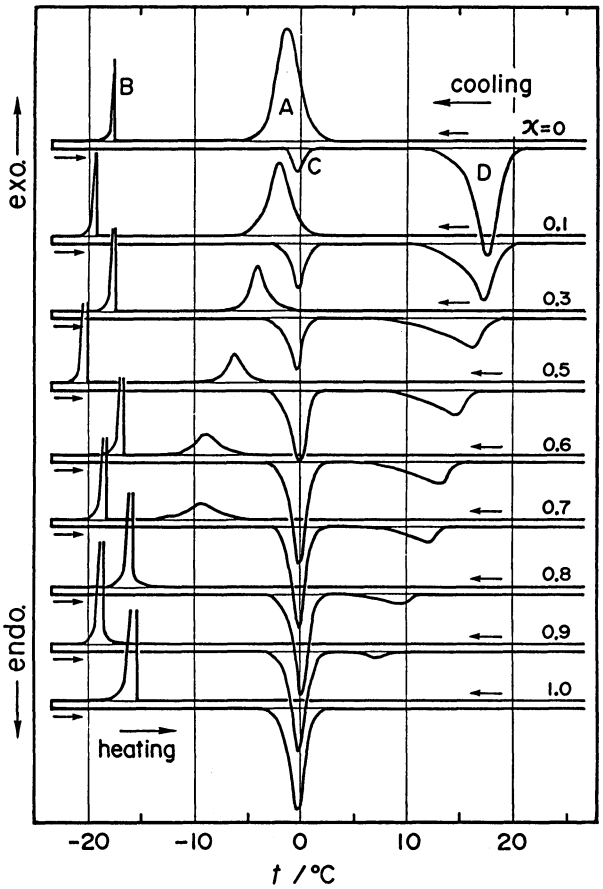

Fig. 1. The DSC signals, expressed in arbitrary units, for aqueous solutions of poly(tetraisopentylammonium acrylate) whose cation is partly replaced with Na^+ ion, $Na_x[(i\text{-}C_5H_{11})_4N]_{1-x}PA$. The numeral attached to each curve stands for the value of x. The mole fraction, based on the monomeric unit, is equal to 0.02 for all the solutions.

Peak **B** indicates the solidification of supercooled water and peak **C** is attributed to the melting of ice. The apparent heat of fusion of the ice phase increases with increasing x, and the dissolution temperature remains almost at around 0 °C, indicating that the effect of the sodium polyacrylate molecule on the formation of ice is fairly slight.

In Fig. 2, two kinds of heat, $\Delta H_1/n_1$ and $\Delta H_1/n_1(1-x)$, are plotted as a function of x. All of the points are averages of 3—6 measurements. The ΔH_1 is the heat absorbed in peak **D** in Fig. 1 and n_1 is the number of moles of the polyacrylate (based on the monomeric unit) contained in each sample solution. Approximately, the quantity $\Delta H_1/n_1$ indicates the apparent heat of fusion of the hydrate solid and $\Delta H_1/n_1(1-x)$ the apparent heat of fusion of the hydrate per one mole of the $(i\text{-}C_5H_{11})_4N^+$ cation. Figure 2 shows that both heats decrease with increasing x. However, the heat $\Delta H_1/n_1(1-x)$ retains a fairly large value within the range x=0—0.5. Furthermore, the apparent hydration numbers, m, estimated by the relation[10] $m=(n_0-\Delta H_0/$

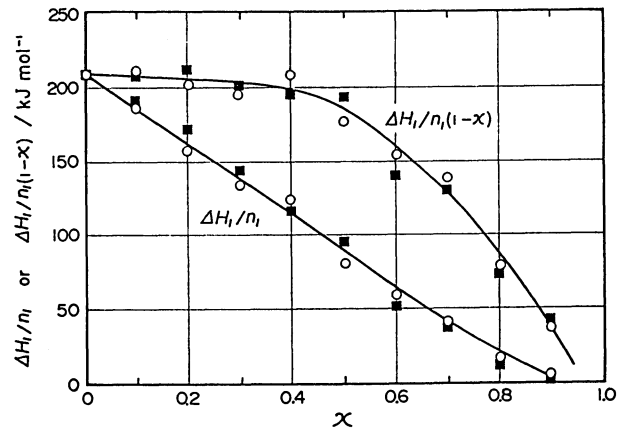

Fig. 2. The x dependence of the apparent enthalpy changes, $\Delta H_1/n_1$ and $\Delta H_1/n_1(1-x)$, in the $Na_x[(i\text{-}C_5H_{11})_4N]_{1-x}PA\text{-}H_2O$ (○) and $[(n\text{-}C_3H_7)_4N]_x[(i\text{-}C_5H_{11})_4N]_{1-x}PA\text{-}H_2O$ (■) systems. ΔH_1 is the total heat of fusion of a hydrate phase and n_1 is the number of moles of polyacrylate anion based on the monomeric unit.

$6.01\times10^3)/n_1$ (in which n_0 is the total number of moles of water in each sample and ΔH_0 is the heat change in the peak **C** in Fig. 1 expressed in Joule unit and 6.01×10^3 is the heat of fusion of ice I at 0 °C), are about 42 at x=0 and retains a value of about 37 at x=0.5. However, when x becomes larger than 0.5, m sharply decreases and becomes about 18 at x=0.9. These facts suggest that the stability of the hydrogen-bonded water networks around the $(i\text{-C}_5\text{H}_{11})_4\text{N}^+$ cation are not so markedly affected by the presence of the Na^+ ion if the number of moles of Na^+ ions does not exceed that of the $(i\text{-C}_5\text{H}_{11})_4\text{N}^+$ ions.

(2) Formation of Hydrate in the $[(n\text{-C}_3\text{H}_7)_4\text{N}]_x[(i\text{-C}_5\text{H}_{11})_4\text{N}]_{1-x}\text{PA-H}_2\text{O}$ Systems. The thermal behaviors of aqueous solutions of poly(tetraisopentylammonium acrylate), whose cation is partly substituted by a $(n\text{-C}_3\text{H}_7)_4\text{N}^+$ ion, are shown in Fig. 3 in a similar manner as in Fig. 1. The curves for x=0.2 and 0.4 were eliminated in order to avoid complexity. The results shown in Fig. 3 clearly indicate that the effect of the $(n\text{-C}_3\text{H}_7)_4\text{N}^+$ ion on the formation of a hydrate is very similar to that of the Na^+ ion shown in Fig. 1: Both the dissolution temperatures of the hydrates and the apparent heat of fusion of the hydrates decrease with increasing x; the heat changes due to the solidification and dissolution of the hydrate phase can be observed even at x=0.9.

The two kinds of heat, $\Delta H_1/n_1$ and $\Delta H_1/n_1(1-x)$, are also plotted against x in Fig. 2. The x dependence of both heats is very much similar to that in the $\text{Na}_x[(i\text{-C}_5\text{H}_{11})_4\text{N}]_{1-x}\text{PA-H}_2\text{O}$ system: The hydrogen-bonded water networks around the $(i\text{-C}_5\text{H}_{11})_4\text{N}^+$ cation are not markedly affected by the presence of a $(n\text{-C}_3\text{H}_7)_4\text{N}^+$ cation at least x is smaller than 0.5.

However, a striking difference between Figs. 1 and 3 can be found in the thermal behaviors of the ice phase: (1) the dissolution temperature of the ice decreases with increasing x from 0 up to 0.5; (2) at x=0.5 solidification of ice occurs at very low temperature (around −26 °C); (3) at x=0.6 the dissolution temperature becomes fairly high compared with that of a solution of x=0.5, and again gradually decreases with increasing x from 0.6 to 1.0; and (4) the apparent heat of fusion remains rather small up to x=0.5, and at x=0.6 it abruptly becomes large but maintains similar values up to x=1.0 (the latter

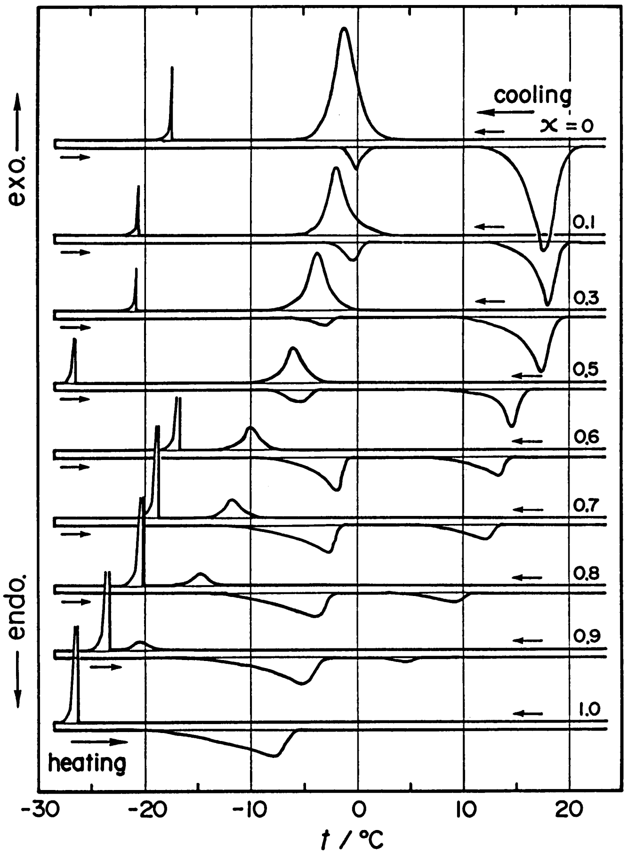

Fig. 3. DSC signals, expressed in arbitrary units, for aqueous solutions of poly(tetraisopentylammonium acrylate) whose cation is partly replaced with $(n\text{-C}_3\text{H}_7)_4\text{N}^+$ ion, $[(n\text{-C}_3\text{H}_7)_4]_x[(i\text{-C}_5\text{H}_{11})_4\text{N}]_{1-x}\text{PA}$. The numeral attached to each curve stands for the value of x. The mole fraction, based on the monomeric unit, is equal to 0.02 for all the solutions.

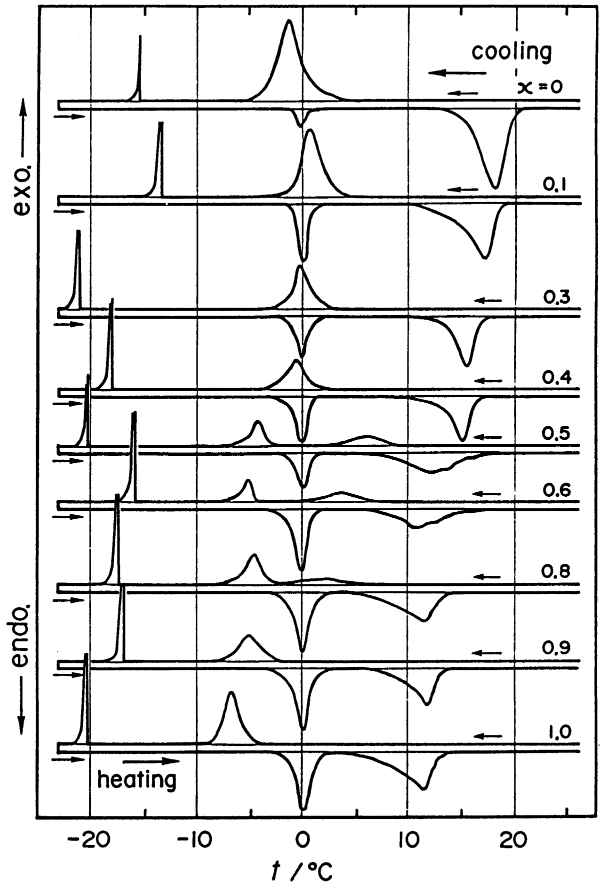

Fig. 4. DSC signals, expressed in arbitrary units, for aqueous solutions of poly(tetraisopentylammonium acrylate) whose cation is partly replaced with the $(n\text{-C}_4\text{H}_9)_4\text{N}^+$ ion, $[(n\text{-C}_4\text{H}_9)_4\text{N}]_x[(i\text{-C}_5\text{H}_{11})_4\text{N}]_{1-x}\text{PA}$. The numeral attached to each curve stands for the value of x. The mole fraction, based on the monomeric unit, is equal to 0.02 for all the solutions.

heat is about 2—4 times of the former). Although a detailed discussion concerning these behaviors of the ice phase is not presently possible, it is clear that the structure of the ice phase is markedly affected by the presence of the $(n\text{-}C_3H_7)_4N^+$ ion, as has often been pointed out elsewhere.[1]

(3) Formation of Hydrate in $[(n\text{-}C_4H_9)_4N]_x[(i\text{-}C_5H_{11})_4N]_{1-x}PA\text{-}H_2O$ Systems. The cooling and heating curves produced from differential scanning calorimetry for aqueous solutions of $[(n\text{-}C_4H_9)_4N]_x[(i\text{-}C_5H_{11})_4N]_{1-x}PA$ are shown in Fig. 4 as a function of x. The mole fractions of all the solutions are equal to 0.02. The characteristic features of the results shown in Fig. 4 can be summarized as follows: (1) With increasing x from 0 to about 0.4, in the cooling process, an exothermic peak due to the solidification of a hydrate phase appears at around 0 °C, regardless of the values of x and both the temperature at which a hydrate phase begins to melt and the dissolution temperature (which is defined as the temperature corresponding to the maximum of the heating curve) gradually decrease; (2) When x becomes larger than 0.5 two exothermic peaks appear in the cooling curve: one of them appears at around −5 °C, regardless of the value of x, whereas the other one is fairly broad and shifts to lower temperatures with increasing x and can no longer be observed in the x=0.9 solution; (3) The heating curves of systems of x greater than 0.5 indicate, at least apparently, that two types of hydrate phases melt successively with increasing temperature, one of which always melts at around 11 °C, and that the melting point of the other one is about 13.5 °C when x=0.5 and gradually decreases with increasing x; the latter hydrate cannot be identified when x is larger than 0.8; (4) The endothermic peaks which may be ascribed to the melting of the ice phase appear around 0 °C, regardless of the value of x, showing a similar result to that shown in Fig. 1 and a striking difference from that shown in Fig. 3.

In Fig. 5, the heat $\Delta H_1/n_1$ and the dissolution temperature t are plotted against x. It is interesting to note that, although both $\Delta H_1/n_1$ and t gradually decrease with increasing x from 0 to about 0.4, they remain almost constant when x is larger than 0.5. These results indicate that the hydrate phase formed when x=0—0.4 is essentially a $(i\text{-}C_5H_{11})_4NPA$ hydrate and its stability is lowered with an increasing amount of the $(n\text{-}C_4H_9)_4N^+$ ion and that the hydrate phase formed when x is larger than 0.5 is essentially a $(n\text{-}C_4H_9)_4NPA$ hydrate, whereas its stability is only slightly affected by the presence of the $(i\text{-}C_5H_{11})_4N^+$ ion. This behavior may

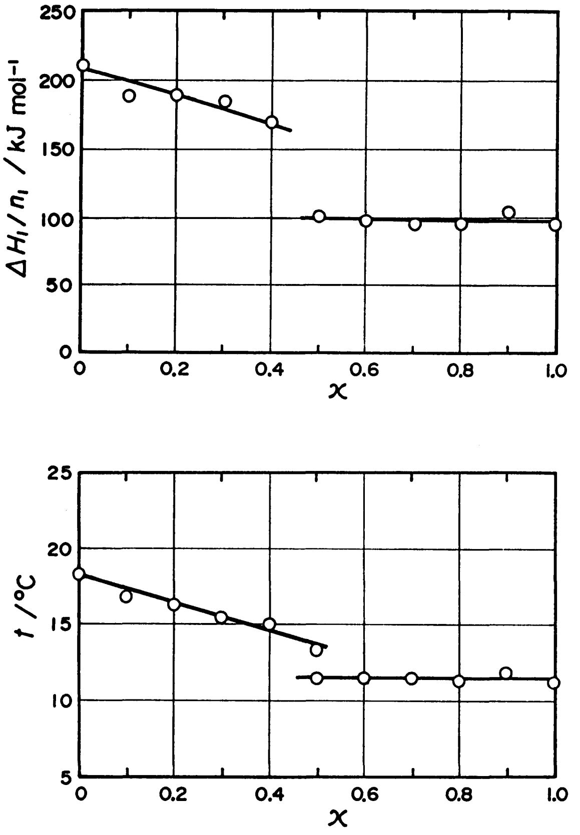

Fig. 5. The x dependence of the apparent enthalpy change $\Delta H_1/n_1$ and the dissolution temperature t in the $[(n\text{-}C_4H_9)_4N]_x[(i\text{-}C_5H_{11})_4N]_{1-x}PA\text{-}H_2O$ system. ΔH_1 and n_1 are the same quantities as those given in Fig. 2.

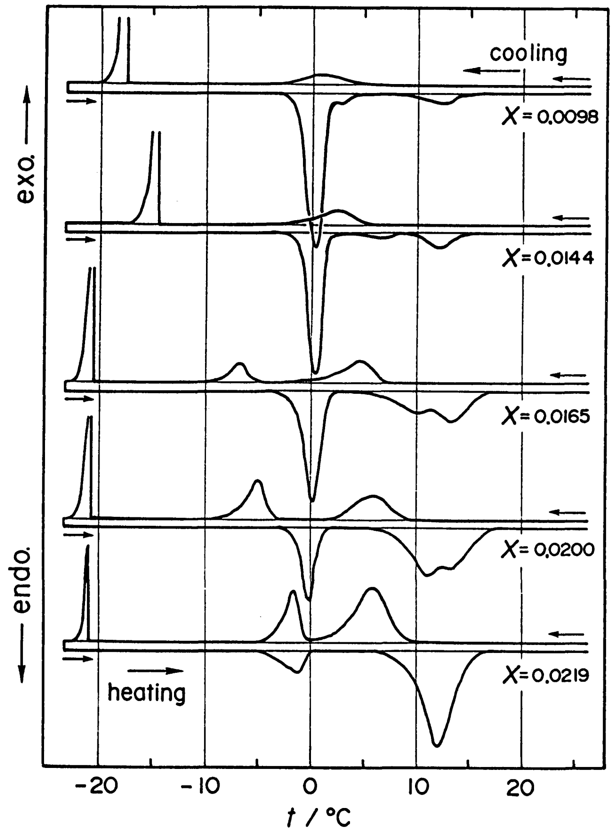

Fig. 6. Concentration dependence of the DSC signals, expressed in arbitrary units, for aqueous solutions of $[(n\text{-}C_4H_9)_4N]_{0.5}[(i\text{-}C_5H_{11})_4N]_{0.5}PA$. The X is the mole fraction of the polyacrylate based on the monomeric unit.

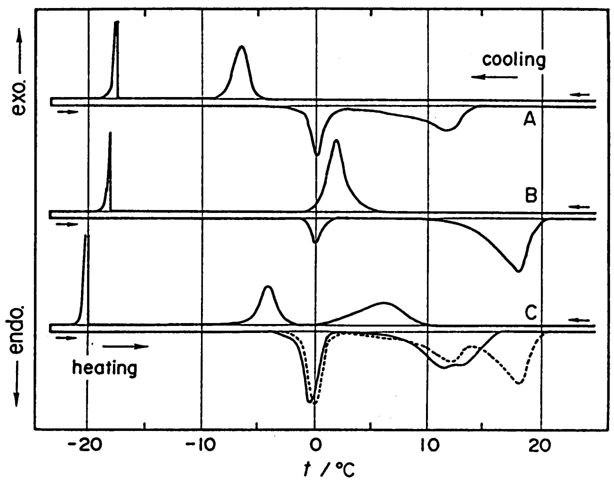

Fig. 7. Sum (dotted line in **C**) of the two heating curves, the heating curve of the (n-$C_4H_9)_4NPA$-H_2O system (curve **A**) and that of the (i-$C_5H_{11})_4NPA$-H_2O system (curve **B**), compared with the heating curve of the $[(n\text{-}C_4H_9)_4N]_{0.5}[(i\text{-}C_5H_{11})_4N]_{0.5}PA$-$H_2O$ system (full line in the curve **C**). The mole fraction of the polyacrylate, based on monomeric units, is equal to 0.02 for the three systems. The peak hights are adjusted so as to contain the same amounts of the (n-$C_4H_9)_4N^+$ ion and the (i-$C_5H_{11})_4N^+$ ion.

be explained by the fact that hydrogen-bonded water networks around the (i-$C_5H_{11})_4N^+$ cation are more stable than those around the (n-$C_4H_9)_4N^+$ cation.[11]

However, the nature of the hydrate phase formed in solutions whose x is neither small nor large (x=0.5 for example) is not clear from the results shown in Figs. 4 and 5. For solutions with x=0.5, the concentration dependence of the thermal behavior is shown in Fig. 6. The mole fraction, X, varies from 0.0098 to 0.0219. Both cooling curves and heating curves undoubtedly indicate that two types of solidification and melting processes are present, although in the cooling curves for fairly dilute solutions (X=0.0098 and 0.014) and in the heating curves for fairly concentrated solution (X=0.0219) the two processes cannot be clearly separated. These two processes seem to indicate the formation of stable hydrogen-bonded water networks around the (i-$C_5H_{11})_4N^+$ cation and (n-$C_4H_9)_4N^+$ cation, respectively.

In Fig. 7, the sum of the two heating curves (dotted line), heating curves of the (n-$C_4H_9)_4NPA$-H_2O (X=0.02) system[11] (curve **A**) and of the (i-$C_5H_{11})_4NPA$-H_2O (X=0.02) system[11] (curve **B**), is compared with that of the $[(n\text{-}C_4H_9)_4N]_{0.5}[(i\text{-}C_5H_{11})_4N]_{0.5}PA$-$H_2O$ (X=0.02) (curve **C**). They are adjusted so as to contain the same amounts of (n-$C_4H_9)_4N^+$ and (i-$C_5H_{11})_4N^+$ ions. It is clear that the two heating curves do not coincide with each other. This fact would suggest that a hydrate phase formed in the $[(n\text{-}C_4H_9)_4N]_{0.5}[(i\text{-}C_5H_{11})_4N]_{0.5}PA$-$H_2O$ systems is not a simple mixture of a (n-$C_4H_9)_4NPA$ hydrate and a (i-$C_5H_{11})_4NPA$ hydrate, but, rather, a uniform hydrate in which both the (n-$C_4H_9)_4N^+$ and (i-$C_5H_{11})_4N^+$ cations are randomly distributed throughout the hydrate solid. The appearance of two exothermic peaks in the cooling process and of two endothermic peaks in the heating process for the hydrate phase in the solution of x=0.5—0.7, shown in Figs. 4 and 6, may be explained by the fact that the stability of the hydrogen-bonded water networks around a (i-$C_5H_{11})_4N^+$ ion is somewhat different from that around a (n-$C_4H_9)_4N^+$ ion, as mentioned above.

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