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Hydrates of Organic Compounds. XVIII.
The Formation of Hydrates of Tetraisopentylammonium Salts Having Polyanions

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In order to confirm the formation of hydrates, both the solid–liquid phase diagrammatic method and the thermal analytic method using a differential scanning calorimeter were applied to binary mixtures of water with various tetraisopentylammonium salts having polyanions, poly(vinyl sulfate) anion and poly(styrenesulfonate) anion, as well as related low molecular-weight anions, ethyl sulfate ion and *p*-ethylbenzenesulfonate ion. It was found that the two salts with the polyanions and ethanesulfate could form hydrates with large hydration numbers: The melting point and hydration numbers were estimated to be around 16.5 °C and 34±2 for the tetraisopentylammonium poly(vinyl sulfate) hydrate; around 11 °C and 35 for the tetraisopentylammonium poly(styrenesulfonate) hydrate; and 12—13 °C and 37±2 for the tetraisopentylammonium ethyl sulfate hydrate, respectively. The formation of the hydrate phase around the tetraisopentylammonium cation attached to a surface of cation-exchange resins was also examined.

In 1987 one of the authors first reported that tetrabutylammonium polyacrylate and tetraisopentylammonium polyacrylate could form fairly stable hydrates having a large number of water molecules per single unit of polyacrylate chain (hydration numbers).[1] The melting points and hydration numbers of these two hydrates were 11.2 °C and 30±1 for the tetrabutylammonium polyacrylate hydrate and 19.5 °C and 42±2 for the tetraisopentylammonium polyacrylate hydrate, respectively. From the facts that these hydrates have fairly high melting points and large hydration numbers, these hydrates were regarded as being clathrate-like hydrates similar to such well-known hydrates as $(n\text{-}C_4H_9)_4NF\cdot(\text{ca. }30)H_2O$[2] and $(i\text{-}C_5H_{11})_4NF\cdot(\text{ca. }40)H_2O$.[3] Furthermore, we very recently reported on the formation of similar types of hydrates of tetrabutylammonium and tetraisopentylammonium poly(ethenesulfonate).[4] One of the most significant characteristics of these polymeric salt hydrates is that their stability (melting point) is fairly high in spite of the unfavorable conditions, in which a long polymeric chain must be regularly accommodated within hydrogen-bonded water networks (host structure). From various experimental results[5—8] the high stability of these hydrates may be ascribed to the fact that hydrogen-bonded water networks can most stably be constructed around either the tetrabutylammonium or tetraisopentylammonium cation.

In this study, we further investigated the possibility of the formation of hydrates of tetraisopentylammonium salts having polyanions which are more bulky and, therefore, are considered to be more unfavorable to hydrate formation than such anions as polyacrylate and poly(ethenesulfonate): tetraisopentylammonium poly(vinyl sulfate) tetraisopentylammonium poly(styrenesulfonate), together with tetraisopentylammonium salts having related low molecular weight anions, vinyl sulfate and ethylbenzenesulfonate. In addition to this, the formation of a hydrogen-bonded water structure around the tetraisopentylammonium cation attached to the negatively charged surfaces of cation-exchange resins was also examined by a thermal analytical method using a differential scanning calorimeter.

Experimental

Materials. All of the aqueous solutions of tetraisopentylammonium poly(vinyl sulfate), $(i\text{-}C_5H_{11})_4N^+[-CH_2-CH(O-SO_2-O^-)-]_n$ (denoted $(i\text{-}C_5H_{11})_4$NPVS hereafter); tetraisopentylammonium poly(styrenesulfonate), $(i\text{-}C_5H_{11})_4N^+[-CH_2-CH(C_6H_4SO_3{}^-)-]_n$ (denoted $(i\text{-}C_5H_{11})_4$ NPSS hereafter); tetraisopentylammonium ethyl sulfate, $(i\text{-}C_5H_{11})_4N^+(CH_3CH_2O-SO_2-O^-)$ (denoted $(i\text{-}C_5H_{11})_4$NES hereafter); and tetraisopentylammonium ethylbenzenesulfonate, $(i\text{-}C_5H_{11})_4NO_3S(C_6H_4)C_2H_5$ (denoted $(i\text{-}C_5H_{11})_4$NEBS hereafter) were prepared by neutralizing an aqueous solution of tetraisopentylammonium hydroxide, $(i\text{-}C_5H_{11})_4NOH$, with the corresponding acid solutions. The aqueous $(i\text{-}C_5H_{11})_4NOH$ solution was obtained by reacting $(i\text{-}C_5H_{11})_4NI$ 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.[6] All of the acid solutions, except for $C_2H_5(C_6H_4)SO_3H$, were obtained by passing each sodium (or pottasium) salt solution through a column of cation-exchange resin (Amberlite IR-120B) converted (in advance) into the acid form by 2 mol dm^{-3} hydrochloric acid solution. Both $C_2H_5(C_6H_4)SO_3H$ and sodium ethylsulfate, $C_2H_5SO_4Na$, were purchased from Tokyo Kasei Kogyo Co., Ltd. and used without further purification. Potassium poly(vinyl sulfate), KPVS, and sodium poly(styrenesulfonate), NaPSS, which were also purchased from Tokyo Kasei Kogyo Co., Ltd., were purified by the following procedure: A concentrated aqueous solution of KPVS was added dropwise into a large amount of ethanol with stirring, followed by filtration of precipitated KPVS. This procedure was repeated three times. The NaPSS was also purified by a similar process using 2-propanol instead of ethanol.

The cation-exchange resins used were of one carboxylate type (DOWEX MWC-1) and two sulfonate types (DOWEX 50W-X2 and IR-120B). The wet cation-exchange resins partially converted into $(i\text{-}C_5H_{11})_4N^+$-form were obtained by passing an aqueous solution of $(i\text{-}C_5H_{11})_4NOH$ through a column of each cation-exchange resin converted (in advance) into the acid form by about 2 mol dm^{-3} hydrochloric acid. Then, each resin was washed with water until the hydroxide ion was no longer detected.

Procedures. The solid(hydrate)–liquid-phase diagram was determined in the following manner. A sample solution (about 1.0 g) was prepared by weighing out water and a concentrated mother solution; it was then sealed in a small glass ampoule. The concentrations of the mother solutions were determined by titration of the tetraisopentylammonium ion with a 0.02 mol dm^{-3} sodium tetraphenylborate solution, which was standardized with a known amount of pure $(n\text{-}C_4H_9)_4NI$. Each ampoule was gradually cooled until the solid phase appeared and was annealed for at least 48 h at a temperature a few degrees lower than the temperature at which the solid phase completely dissolved. After that, the ampoule was slowly warmed (at a 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.

The solid (which may be anhydrous salt)–liquid phase diagrams were determined by measuring the solubility of the salt in water at various temperatures. In a measuring cell (3 cm diameter and 10 cm high) immersed in a constant-temperature bath the solid sample was saturated in 10—20 cm^3 of water by vigorous stirring with a magnetic stirrer for 2—10 h. Then, a given amount of each saturated solution was withdrawn and analyzed by the titration method mentioned above.

The liquid–liquid phase diagrams were determined by measuring the temperature at which the separation into two liquid phases occurred when an aqueous solution sealed in an ampoule was gradually heated.

The differential scanning calorimeter used was a model DSC10 with an SSC580 thermal controller manufactured by Seiko Instruments and Electronics Ltd. Either sample solutions (about 15 mg) at various concentrations or ion-exchange resins partially converted into the $(i\text{-}C_5H_{11})_4N^+$-form were sealed in a 15 μl aluminum pan. The DSC signal was measured by either cooling or heating the sample as slowly as possible (usually at a rate of 0.5 °C per minute). An empty 15 μl aluminum pan was used as a reference.

Results and Discussion

(1) The Formation of Hydrates of Tetraisopentylammonium Poly(vinyl sulfate). The solid–liquid and liquid–liquid phase diagrams for the binary systems, water–$(i\text{-}C_5H_{11})_4NPVS$ (**I**), are shown in Fig. 1, together with the solid–liquid phase diagram for the related low-molecular weight system: water–$(i\text{-}C_5H_{11})_4NES$ (**II**). The logarithm of the concentration expressed as the mole fraction (based on the monomeric unit), X, is plotted against the reciprocal of the absolute temperature. The solid–liquid phase diagrams below 16.2 °C for system **I** and those below 11.5 °C for system **II** clearly indicate the formation of hydrates containing a large number of water molecules per one $(i\text{-}C_5H_{11})_4N^+$ cation (hydration numbers), based on the fact that the slopes of these two curves $(-\partial \log X/\partial(1/T))$ are almost the same as those previously found for various tetraisopentylammonium hydrates:[6,7,9] It has been verified that this slope is approximately proportional to the hydration numbers.[7] The formation of hydrates for systems **I** and **II** has not been reported before. The melting points are estimated to be around 16.5 °C for the $(i\text{-}C_5H_{11})_4NPVS$ hydrate and 12—13 °C for the $(i\text{-}C_5H_{11})_4NES$ hydrate, though exact values cannot be determined, since the hydrate–solution equilibrium curve intersects with the liquid–liquid equilibrium curve at around 16.2 °C in system **I** and with another solid (which seems to be anhydrous solid)–solution equilibrium curve at around 11.5 °C in system **II**.

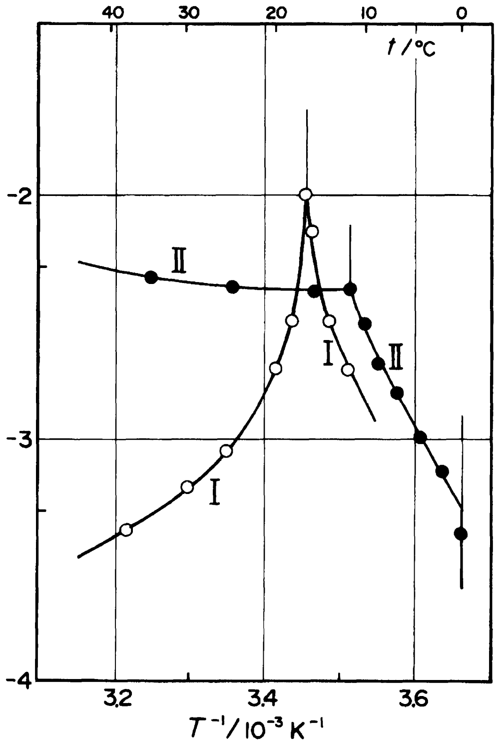

Fig. 1. Solid–liquid and liquid–liquid phase diagrams for the $(i\text{-}C_5H_{11})_4NPVS$–water (**I**) and the $(i\text{-}C_5H_{11})_4NES$–water (**II**) systems.

In Fig. 2, the cooling and heating curves in the differential scanning calorimetry (DSC) for aqueous solutions of $(i\text{-}C_5H_{11})_4NPVS$ (a) and of $(i\text{-}C_5H_{11})_4NES$ (b) are shown as a function of the temperature for solutions of X=0.003, 0.007, and 0.01 for the former salt and X=0.004 for the latter. It is obvious that in the cooling process exothermic peaks in the −10—−20 °C range indicate the solidification of supercooled water; in the heating process, endothermic peaks in the −5—0 °C range are attributable to melting of the ice phase. Thus, the other exothermic peaks at around −5—−10 °C in the cooling process and exothermic

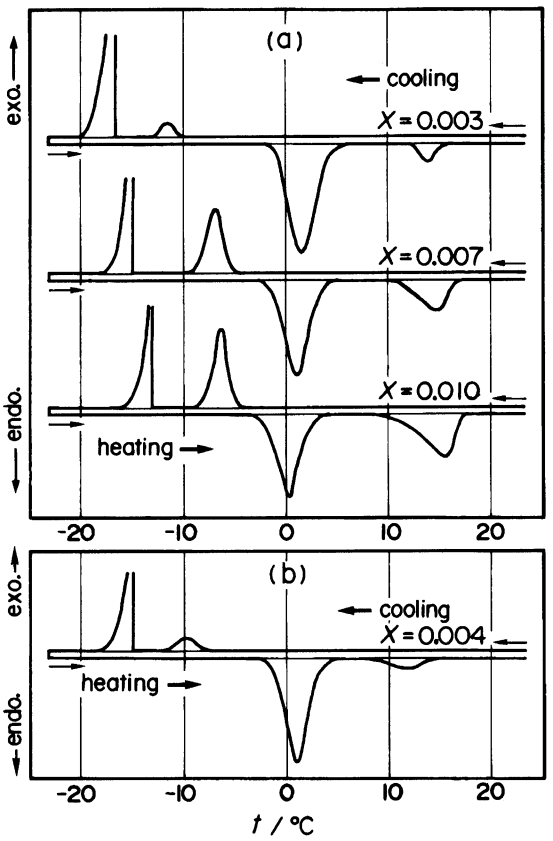

Fig. 2. Temperature dependence of the DSC signals, expressed in an arbitrary unit, for aqueous solutions of (i-$C_5H_{11})_4$NPVS (a) and of (i-$C_5H_{11})_4$NES (b). X is the mole fraction of the salt.

peaks at around 10—15 °C indicate a solidification and melting of the hydrate phase discussed above. Using the observed enthalpies of fusion of both the ice phase and the hydrate phase and the previously proposed relationship,[10] the hydration numbers were estimated to be 34±2 for the (i-$C_5H_{11})_4$NPVS hydrate and 37±2 for the (i-$C_5H_{11})_4$NES hydrate. These values are somewhat smaller than those for typical hydrates, such as (i-$C_5H_{11})_4$NF hydrate and (i-$C_5H_{11})_4$NCl hydrate: around 40.[6,7] A detailed discussion concerning the hydration numbers is impossible since DSC measurements are possible only for dilute solutions whose concentrations are far from the expected congruent composition. It has been known that the estimation of the hydration numbers from the DSC measurements becomes inaccurate for dilute solutions.[1,10]

(2) Formation of the Hydrates of Tetraisopentylammonium Poly(styrenesulfonate). The solid–liquid and liquid–liquid phase diagrams for the binary systems, water–(i-$C_5H_{11})_4$NPSS (**I**), are shown in Fig. 3, together with those for the water–(i-$C_5H_{11})_4$NEBS (**II**). The solid–liquid equilibrium line for system **I** clearly indicates the formation of a hydrate having similar characteristics to those of the (i-$C_5H_{11})_4$NPVS hydrate mentioned above. The formation of the (i-$C_5H_{11})_4$NPSS hydrate was first confirmed in this study. Since the solid–liquid equilibrium curve intersects the liquid–liquid equilibrium curve at a concentration of around X=0.015, the exact melting point and hydration numbers of this hydrate cannot be determined. However, from this phase diagram, the melting point of the (i-$C_5H_{11})_4$NPSS hydrate may be estimated to be around 11 °C. Figure 3 also shows that the corresponding low-molecular weight salt, (i-$C_5H_{11})_4$NEBS, cannot form any hydrate. The solid (which seems to be anhydrous)–liquid equilibrium line intersects the liquid–liquid equilibrium line at around 37 °C.

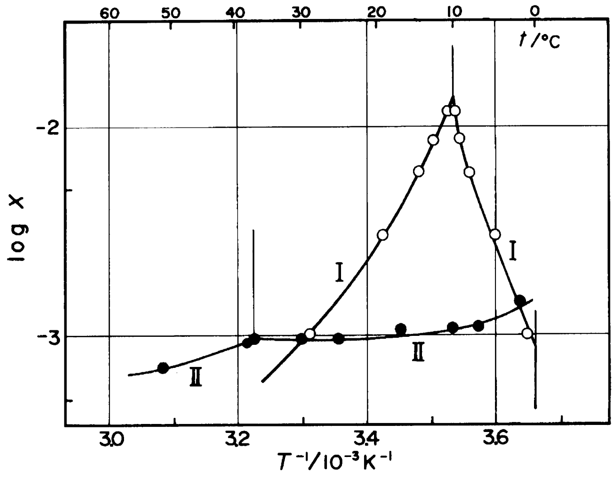

Fig. 3. Solid–liquid and liquid–liquid phase diagrams for the (i-$C_5H_{11})_4$NPSS–water (I) and (i-$C_5H_{11})_4$NEBS–water (II) systems.

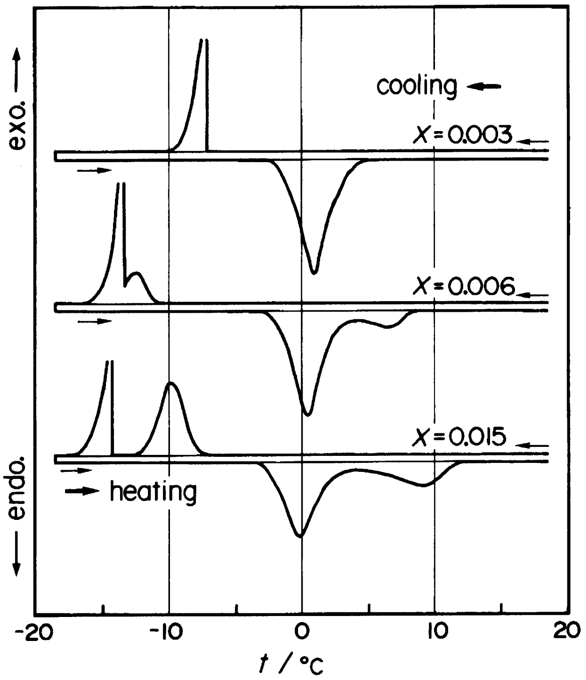

Fig. 4. Temperature dependence of the DSC signals, expressed in an arbitrary unit, for aqueous solutions of (i-$C_5H_{11})_4$NPSS. X is the mole fraction of the salt.

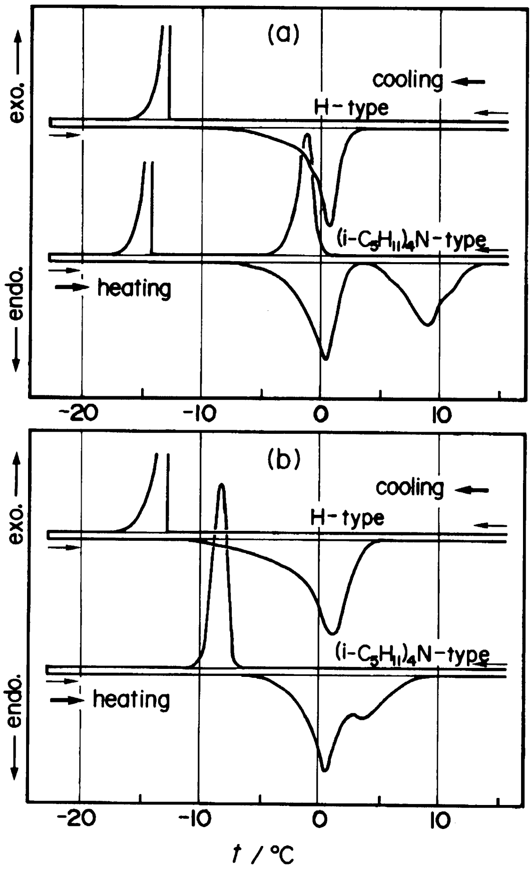

Fig. 5. Temperature dependence of the DSC signals, expressed in an arbitrary unit, for wet cation-exchange resins converted into acid form and partially converted into $(i\text{-}C_5H_{11})_4N^+$-form for two types of resins, DOWEX MWC-1 (a) and DOWEX 50W-X2 (b).

In Fig. 4, the cooling and heating curves in the DSC measurements for aqueous solutions of $(i\text{-}C_5H_{11})_4$NPSS are shown in a similar manner as in Fig. 2. Detailed DSC measurements for this system cannot be made, since the concentration of the sample is limited in fairly dilute solutions. However, the heating curves for a solution of $X=0.006$ and $X=0.015$ as well as the cooling curve for the $X=0.015$ solution clearly indicate the formation of a solid phase other than an ice phase. It is obvious from the phase diagram shown in Fig. 3 that this solid phase corresponds to the hydrate phase. The hydration numbers of this hydrate may be estimated to be around 35 from the heating curve of the $X=0.015$ solution using the previously proposed relationship.10)

(3) Formation of Hydrates of Tetraisopentylammonium Salts on the Surface of Cation-Exchange Resins. In Fig. 5, the cooling and heating curves in the differential scanning calorimetry are given for wet cation-exchange resins converted into the acid form and partially converted into the $(i\text{-}C_5H_{11})_4N^+$-form for two types of resins, DOWEX MWC-1 (a) and DOWEX 50W-X2 (b). The degree of conversion of the $(i\text{-}C_5H_{11})_4N^+$ ion was estimated to be about 65% for the former resin and about 80% for the latter resin. Figure 5 clearly indicates the formation of a solid phase other than ice in both $(i\text{-}C_5H_{11})_4N^+$-form resins. The temperature corresponding to the highest endothermic peak is around 8 °C for the MWC-1 system and around 4 °C for the 50W-X2 system. Though there is not detailed information concerning the nature of these solid phases, it would be reasonable to expect that this solid pahse is a hydrate phase formed around the $(i\text{-}C_5H_{11})_4N^+$ cation attached to either the COO^- group or the $SO_3{}^-$ group of the cation-exchange resins. Such a hydrate phase cannot be detected in a system containing the IR-120B resin. This may be, at least in part, attributed to the fact that the degree of exchange of the $(i\text{-}C_5H_{11})_4N^+$ cation is fairly low (less than 50%) because of the high degree of cross-linkage of the IR-120B resin.

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