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THE MEASUREMENT OF HEAT CAPACITY DIFFERENCES DUE TO THE CHANGE OF WATER STRUCTURE IN AQUEOUS SOLUTIONS OF ORGANIC COMPOUNDS

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Abstract

In order to observe more directly the structural organization of water molecules around a nonpolar molecule in an aqueous solution, heat capacity differences between two kinds of solutions (solution I and II) of quaternary ammonium salts were measured. In the solution I stable water structure was retained as much as possible and in the solution II water structure was destroyed either by heating to high temperatures or by irradiating with ultrasonic waves. It was found that the heat capacity differences ($(C_p)_{II}-(C_p)_I$) were slightly positive and its maximum values corresponded to 7–8 percent of the heat capacity of pure water itself.

Keywords: differential scanning calorimetry, heat capacity, hydrophobic hydration, quaternary ammonium salts

Introduction

Recently, we proposed a new experimental method to observe more directly the state of hydrogen-bonded water networks around nonpolar molecules [1–4]. The principle of our new method is based on the observation of the differences of various properties between two kinds of solutions (solution I and II). The solution I is a solution in which stable hydrogen-bonded water structure is retained as much as possible by keeping at low temperatures, and solution II is a solution whose water networks are destroyed deliberately either by raising to high temperatures [1, 3] or by irradiating with ultrasonic waves [2]. In carrying out these types of experiments, important two factors should be determined in advance: (1) appropriate solute molecules to use; and (2) appropriate physical properties to measure.

In our previous study, we used two quaternary ammonium salts, $(n\text{-}C_4H_9)_4NCl$ and $(i\text{-}C_5H_{11})_4NCl$ as solute molecules. The reason why we chose $(n\text{-}C_4H_9)_4NCl$ and $(i\text{-}C_5H_{11})_4NCl$ as solute molecules is as follows: It is well-known that these tetraalkylammonium salts can form unusual hydrates having a large number of water molecules per ammonium ion (hydration numbers) and fairly high melting points (the hydration numbers are around 30) for the $(n\text{-}C_4H_9)_4NCl$ hydrate and around 40 for the $(i\text{-}C_5H_{11})_4NCl$ hydrate; the melting points are 15.0 and 29.6°C, respectively [5].

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These hydrates are of the semi-clathrate type [6, 7], similar to the so-called gas hydrates: the water structure is a hydrogen-bonded network (polyhedron) and each alkyl group of an ammonium cation is incorporated into one of the polyhedra. It was found in our previous study [8] that the enthalpies of solution in a saturated aqueous solution of clathrate-like hydrate solids of these ammonium salts corresponded to about 90% of the enthalpies of fusion of these hydrate solids. This fact clearly suggests that the state of the hydrogen-bonded water networks around the alkyl chains, like n-C_4H_9 and i-C_5H_{11} in an aqueous solution, is very much similar to that in the melt of these hydrates: A stable hydrogen-bonded water structure around the alkyl chain in the hydrate solid remains in its aqueous solution to a great extent.

As measuring properties we employed supercooling temperatures and enthalpies of mixing with some solvents in our previous study [1–4]. It was found that the supercooling temperatures of the solution I were higher than those of the solution II, and that enthalpies of mixing of the solution I were more endothermic than those of the solution II. From these results it was concluded that these tetraalkylammonium salts were appropriate solutes and such properties as supercooling temperatures and enthalpies of mixing with some solvents were appropriate quantities to observe the difference in the stabilities of the hydrogen-bonded water networks in these two solutions. In addition, these results indicate the fact that thermally destroyed hydrogen-bonded water networks in the solution II cannot easily revert to a state in the solution I within the time interval examined.

In this study, similar types of experiments were carried out in order to determine whether such a difference can also be detected by heat capacity measurements.

Experimental

Aqueous solutions of tetrabutylammonium chloride and tetraisopentylammonium chloride were prepared by a similar manner as described before [1, 2, 4]. The concentrations of the mother solutions of these two chlorides were determined by titration of the corresponding ammonium ion with a 0.02 mol dm^{-3} sodium tetraphenylborate solution, which had been standardized with a known amount of pure $(n\text{-}C_4H_9)_4NI$.

Based on the hydrate solid – liquid phase diagrams of the binary systems of $(n\text{-}C_4H_9)_4NCl\text{–}H_2O$ and $(i\text{-}C_5H_{11})_4NCl\text{–}H_2O$, which were obtained in a previous experiment [1], six solutions were chosen as being appropriate for carrying out this experiment. These solutions are listed in Table 1 together with the dissolution temperatures (t's) at which the hydrate solid phase completely disappeared when the hydrate solid-aqueous solution equilibrium mixture was gradually heated.

To each solution listed in Table 1 the following procedures were applied. By repeated cooling and heating of the solution a well-formed hydrate crystal, either $(n\text{-}C_4H_9)_4NCl\cdot(\text{ca. }30)H_2O$ or $(i\text{-}C_5H_{11})_4NCl\cdot(\text{ca. }40)H_2O$, was formed. Then three kinds of solutions (solutions I, II, and II′) were prepared: Solution I was prepared by melting the hydrate crystal at a temperature only one degree higher than its dissolution temperature (listed in Table 1); Solution II was prepared by heating the solution

I up to 80°C (or 150°C); solution II′ was prepared by irradiating solution I with ultrasonic waves (38 kHz) for 5 min at the same temperature as the solution I.

Table 1 Mole fractions X and the dissolution temperatures t of the aqueous solutions used in this experiment

Salt	X	t/°C
$(n\text{-}C_4H_9)_4NCl$	0.01	10.3
	0.02	13.8
$(i\text{-}C_5H_{11})_4NCl$	0.003	23.9
	0.006	26.4
	0.01	28.5
	0.02	29.2

For a pair of solutions, either solution I and solution II or solution I and solution II′, heat capacity differences, ΔC_p, were measured by using differential scanning calorimeter. For the measurements of the differences of C_p, ΔC_p, the use of differential scanning calorimeter is the most appropriate. The calorimeter used was model DSC-10 with a SC-580 thermal controller, manufactured by Seiko Instruments and Electronics. Each sample solution (6–13 mg) was sealed in a 15 μl aluminum pan and solution I was set on a reference side and solution II (or solution II′) was set on a sample side. A pair of solutions were heated at a rate of 3 K min^{-1} from 298 to 353 K and all the heat capacity data were determined at 320 K. The observed values of ΔC_p were corrected by carrying out a similar experiment for a standard sample of sapphire. These experimental procedures are illustrated in Fig. 1.

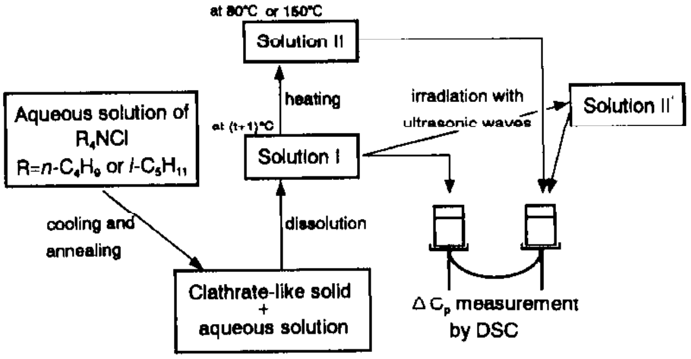

Fig. 1 Schematic presentation for the preparation of solutions I, II and II′ and for the measurements of heat capacity differences

For a pair of solutions, solution I and solution II (or II′), the heat capacity differences, $\Delta C_p=(C_p)_{II}-(C_p)_I$, were determined by the following procedure. The deviation from a base line, h, can be expressed by

$$h=\left\{\frac{\mathrm{d}H(\text{solution}+\text{cell})_{\mathrm{II}}}{\mathrm{d}T}-\frac{\mathrm{d}H(\text{solution}+\text{cell})_{\mathrm{I}}}{\mathrm{d}T}\right\}\frac{\mathrm{d}T}{\mathrm{d}t}=\{m_{\mathrm{II}}(C_{\mathrm{p}})_{\mathrm{II}}-m_{\mathrm{I}}(C_{\mathrm{p}})_{\mathrm{I}}\}\frac{\mathrm{d}T}{\mathrm{d}t}+h'$$

$$\text{where } \frac{\mathrm{d}T}{\mathrm{d}t} \text{ is a heating rate, } h'=\left\{\frac{\mathrm{d}H(\text{cell})_{\mathrm{II}}}{\mathrm{d}T}-\frac{\mathrm{d}H(\text{ cell})_{\mathrm{I}}}{\mathrm{d}T}\right\}\frac{\mathrm{d}T}{\mathrm{d}t},$$

m_{I} and m_{II} are masses of solution I and II, $(C_{\mathrm{p}})_{\mathrm{I}}$ and $(C_{\mathrm{p}})_{\mathrm{II}}$ is heat capacity of solution I and II per unit mass, respectively.
Then we obtain

$$\frac{h-h'}{m_{\mathrm{I}}\frac{\mathrm{d}T}{\mathrm{d}t}}=\frac{\Delta m}{m_{\mathrm{I}}}(C_{\mathrm{p}})_{\mathrm{II}}+\Delta C_{\mathrm{p}},\ \text{where } \Delta m=m_{\mathrm{II}}-m_{\mathrm{I}}$$

In these experiments, the values of h' were measured in advance and then the values of h were measured for a pair of solutions I and II, for which the mass differences, Δm, were varied deliberately in the range of –6 mg to +6 mg. Then the observed values of $(h-h')/m_{\mathrm{I}}\,\mathrm{d}T/\mathrm{d}t$ *vs.* Δm and exact values of ΔC_{p} were obtained by reading the values of the ordinate at $\Delta m=0$.

Results and discussion

In Fig. 2 the observed values of $(h-h')/m_{\mathrm{I}}\,\mathrm{d}T/\mathrm{d}t$ for solution II of $(n\text{-}C_4H_9)_4NCl$ with $X=0.01$ *vs.* Δm, together with similar data for pure water. Both lines are drawn by the least squares method. The line for pure water is drown by passing through zero when $\Delta m=0$ assuming that the heat capacity of pure water at 320 K is inde-

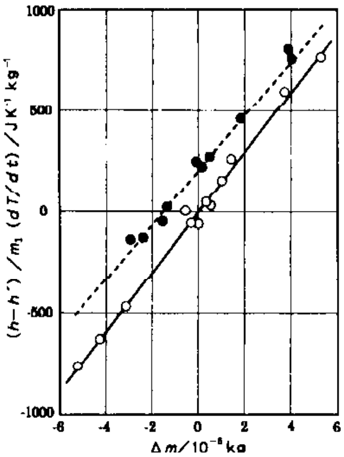

Fig. 2 Relationship between the observed values of $(h-h')/m_{\mathrm{I}}(\mathrm{d}T/\mathrm{d}t)$ and $\Delta m=m_{\mathrm{II}}-m_{\mathrm{I}}$ for aqueous solutions of $(n\text{-}C_4H_9)_4NCl$ with $X=0.01$ (•) and for pure water (o)

pendent of whether it is heated to 80°C in advance or not. The line for the solution II of $(n\text{-}C_4H_9)_4NCl$ is shifted to the same extent as the line of pure water.

From Fig. 2 the $(h - h')/m_I dT/dt$ values at $\Delta m=0$ is determined to be 207 J K^{-1} per kilogram of the solution. This value corresponds to $\Delta C_p=4.3$ J K^{-1} per mole of water if we assume that heat capacity differences are attributable to the structure difference of water molecules: The heat capacity due to the presence of the $(n\text{-}C_4H_9)_4NCl$ molecule is assumed to be identical in solution I and solution II.

Similar data for the solution II of $(i\text{-}C_5H_{11})_4NCl$ with $X=0.01$ are shown in Fig. 3 in the same way as in Fig. 2. For this solution the value of ordinate at $\Delta m=0$ is equal to 224 J K^{-1} per kilogram of the solution: This value corresponds to $\Delta C_p=4.8$ J K^{-1} per mole of water on the basis of the same assumption mentioned above.

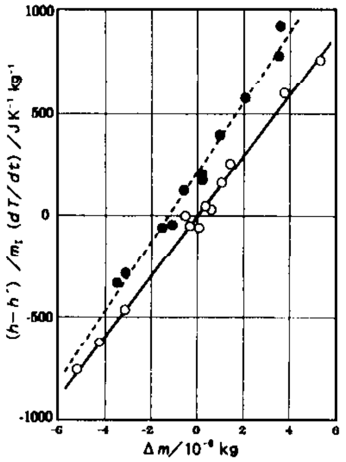

Fig. 3 Relationship between the observed values of $(h-h')/m_I(dT/dt)$ and $\Delta m=m_{II}-m_I$ for aqueous solutions of $(i\text{-}C_5H_{11})_4NCl$ with $X=0.01$ (●) and for pure water (○)

The concentration dependence of the ΔC_p values, which are determined by the same assumption, is shown in Fig. 4 for both $(n\text{-}C_4H_9)_4NCl$ and $(i\text{-}C_5H_{11})_4NCl$ solutions. This figure indicates that the ΔC_p values increase with increasing the concentration and reach maximum values around 5.6 J K^{-1} mol^{-1} for the $(i\text{-}C_5H_{11})_4NCl$ solution and around 5.0 J K^{-1} mol^{-1} for the $(n\text{-}C_4H_9)_4NCl$ solution. These values correspond to 7–8 percent of the heat capacity of pure water itself. The concentrations at which ΔC_p values reach maximum nearly correspond to the congruent composition in the phase diagrams for binary systems of water+$(i\text{-}C_5H_{11})_4NCl$ and water+ $(n\text{-}C_4H_9)_4NCl$, respectively. This composition was shown by a dotted line in Fig. 4. It is interesting to note that the values of ΔC_p for the $(i\text{-}C_5H_{11})_4NCl$ solution is larger than that of the $(n\text{-}C_4H_9)_4NCl$ solution. This fact seems to indicate that the hydrogenbonded water networks around a $(i\text{-}C_5H_{11})_4NCl$ molecule are more stable than those around a $(n\text{-}C_4H_9)_4NCl$ molecule, in good agreement with our earlier conclusion [8].

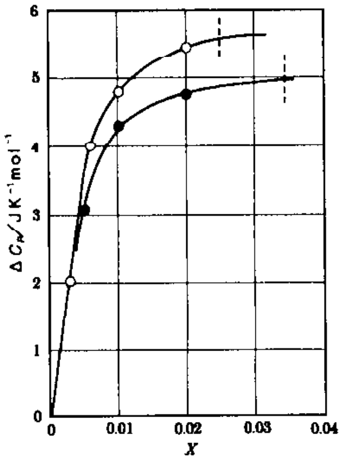

Fig. 4 Concentration dependence of the observed heat capacity differences of water. X is mole fraction of $(n\text{-}C_4H_9)_4NCl$ (•) and of $(i\text{-}C_5H_{11})_4NCl$ (o)

In Fig. 5, similar data are shown for aqueous solutions of $(i\text{-}C_5H_{11})_4NCl$ (with X=0.01) whose solution II is heated up to 150°C. It is interesting to note that ΔC_p values are almost the same for the solutions heated up to 80°C (Fig. 3). This fact indicates that the heating procedure to 80°C is strong enough to destroy the hydrogen-bonded water networks around the quaternary ammonium salt molecules.

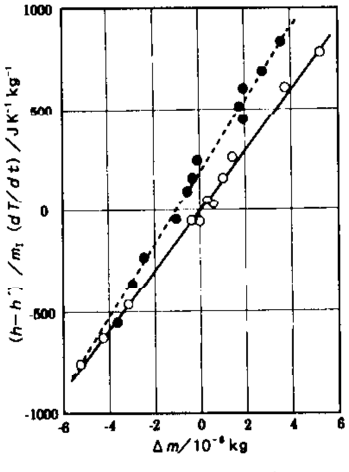

Fig. 5 Relationship between the observed values of $(h-h')/m_I(dT/dt)$ and $\Delta m=m_{II}-m_I$ for aqueous solutions of $(i\text{-}C_5H_{11})_4NCl$ with X=0.01 (•) and for pure water (o). Solution II was prepared by heating to 150°C

In Fig. 6, similar results for $(n\text{-}C_4H_9)_4NCl$ aqueous solutions (with X=0.01) whose water structure is destroyed by irradiation with ultrasonic waves (38 kHz, 5 min). The ΔC_p value obtained for this system is equal to 1.4 J K^{-1} per mole of water. In addition, from similar experiments ΔC_p value for the $(n\text{-}C_4H_9)_4NCl$ aqueous solution with X=0.02 is determined to be 2.0 J $K^{-1}mol^{-1}$. These values are fairly smaller than those observed for the solutions which were heated up to 80°C (4.8 J $K^{-1}mol^{-1}$ for X=0.02, as mentioned above). This phenomena will correspond to the fact that the differences of enthalpies of mixing for the $(n\text{-}C_4H_9)_4NCl$ solutions which are heated up to 80°C are almost three times larger than those observed for the solutions which are irradiated with ultrasonic waves (38 kHz, 20 min) [2].

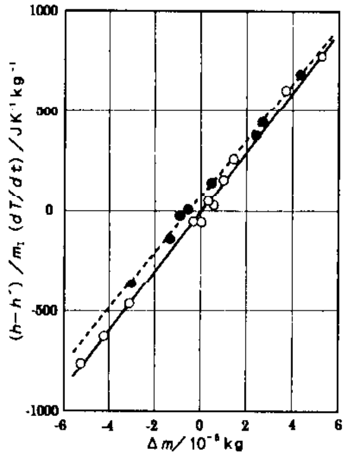

Fig. 6 Relationship between the observed values of $(h-h')/m_I(dT/dt)$ and $\Delta m=m_{II}-m_I$ for aqueous solutions of $(n\text{-}C_4H_9)_4NCl$ with X=0.01 (•) and for pure water (o). Solution II was prepared by irradiating with ultrasonic waves

Although the observed heat capacity differences cannot be discussed in detail at present, it is important to note that energetic information about the hydrogen-bonded water networks around a nonpolar molecule has actually been obtained.

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