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Studies on the hydrophobic hydration by the measurements of supercooling temperature and enthalpies of mixing[1]

Haruo Nakayama*, Yasumasa Tanaka, Hironori Tanimoto

Division of Materials Science and Chemical Engineering, Faculty of Engineering, Yokohama National University, 156 Tokiwadai, Hodogaya-ku, Yokohama 240, Japan

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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, supercooling temperatures and enthalpies of mixing with some organic solvents were measured using two kinds of aqueous solutions (solution I and II) of tetrabutylammonium chloride. Solution I was prepared by melting a hydrate solid formed from the ammonium salt and water, and by keeping its temperature only 1° higher than its dissolution temperature; solution II was prepared by adding urea into solution I at the same temperature by keeping the molar ratio of urea to water as 1 : 49. Supercooling temperatures of solution I were found to be about 20° higher than those of solution II. The differences in enthalpies of mixing between solution I and solution II, $\Delta H_I - \Delta H_{II}$, were found to be about 0.17 kJ/mol of water regardless of the kind of solvents. It has been concluded that these directly reflect the difference in the stability of hydrogen-bonded water networks around a butyl chain of the ammonium cation in aqueous solutions. © 1998 Elsevier Science B.V.

Keywords: Enthalpy of mixing; Hydrophobic hydration; Supercooling temperature; Tetrabutylammonium chloride

1. Introduction

It is well known that nonpolar molecules, such as hydrocarbon molecules, can increase the structural organization of water [1,2] (hydrophobic hydration). This organizing ability of a nonpolar substance on water molecules has been discussed on the basis of indirect thermodynamic information, such as the temperature dependence of solubilities in water, partial molar volumes and heat capacities.

Recently, we proposed a new experimental method to observe the state of hydrogen-bonded water networks around nonpolar molecules more directly [3–5]. The principle of our new method is based on the observation of the differences of various properties between two kinds of solutions (solutions I and II). The solution I is a solution in which hydrogen-bonded water networks are retained as much as possible by keeping at low temperatures, and the solution II is a solution in which water networks are destroyed deliberately, by raising to high temperatures. In carrying out this type of experiments, the following three factors should be determined in advance: (1) an appropriate property to measure; (2) a method to destroy the water structure; and (3) an appropriate solute molecule to use.

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*Corresponding author. Tel.: 0081 045 335 1451; fax: 0081 045 338 3120.

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In our previous study, we used supercooling temperatures and enthalpies of mixing with some solvents as appropriate properties [3–5], and raising to high temperatures [3,5], irradiation with ultrasonic waves [4], and liquid–liquid phase separation process [5] as the methods of destroying water structure. As appropriate solute molecules, we used two quaternary ammonium salts, $(n\text{-}C_4H_9)_4NCl$ and $(i\text{-}C_5H_{11})_4NCl$ [3,4] together with such organic molecules as tetrahydrofuran, isopropyl alcohol and ethyleneglycol butylether [5].

In this study, similar type of experiments were carried out for aqueous solutions of $(n\text{-}C_4H_9)_4NCl$ by destroying the water structure by the addition of urea. Although the effect of addition of urea on water structure is not completely established, urea is considered to act as a structure breaker. Simple model proposed by Frank and Franks [6] suggests that urea dissolves in regions of dense nonhydrogen-bonded water because it is debarred from entering the tetrahedrally hydrogen-bonded clusters owing to its plane triangular shape. Furthermore, by the measurement of ^{14}N relaxation rates for urea it has been concluded that long-range order characteristic for pure water is partly destroyed by introducing urea molecules, indicating breakage of hydrogen bonds [7].

As an appropriate solute molecule we used tetrabutylammonium chloride ($(n\text{-}C_4H_9)_4NCl$). It is known that this molecule can form unusual hydrate having large hydration numbers (around 30) and fairly high melting point (15.0°C) [8]. According to a single-crystal X-ray examination by Jeffrey et al. [9], this hydrate was of semi-clathrate type, similar to the so-called gas hydrates [10], the water structure is a hydrogen-bonded framework and is essentially a regular arrangement of polyhedra. Each butyl group of the $(n\text{-}C_4H_9)_4N^+$ cation is incorporated into one of the polyhedra. In our previous study [11], it was found that enthalpy of solution of the hydrate solid, $(n\text{-}C_4H_9)_4NCl(\text{ca. }30)H_2O$ in a saturated aqueous solution corresponded to about 90% of the enthalpy of fusion of the hydrate solid, and further, that this enthalpy of fusion was approximately equal to the product of the hydration numbers of the hydrate and the molar heat of fusion of ice I. This fact clearly suggests that the state of the hydrogen-bonded water networks around the $n\text{-}C_4H_9$ chains are quite similar to those in the melt of the hydrate: A stable hydrogen-bonded water structure around the $n\text{-}C_4H_9$ chain in the hydrate solid remains in its aqueous solution to a great extent.

2. Experimental

Tetrabutylammonium chloride was prepared by a similar manner as described before [3–5]. The concentration of mother solution of tetrabutylammonium chloride was determined by measuring the amount of tetrabutylammonium cation by titration with a sodium tetraphenylborate solution standardized by pure tetrabutylammonium iodide solid. Other reagents were extra pure reagent grade and used without further purification. The solid–liquid phase diagrams for the ternary systems of water–urea–tetrabutylammonium chloride were determined in the same manner as described in a previous paper [3]. The differential scanning calorimeter used was model DSC-10 with a SC-580 thermal controller, manufactured by Seiko Instruments and Electronics. Each sample solution (ca. 15 mg) was sealed in a 15 μl aluminium pan and was either cooled or heated at a rate of 0.5 K min^{-1}. An empty 15 μl aluminium pan was used as a reference. The calorimeter used was a twin-type conduction calorimeter manufactured by Tokyo Riko (TCC-21). About 0.2 g of each solution, which was sealed in a glass ampoule, was mixed with 25 ml of solvent. An ampoule containing 0.2 g of the solvent was used as a reference.

The total schema of the experimental procedures are illustrated in Fig. 1. By repeated cooling and heating of the sample solution a well-formed hydrate crystal, $(n\text{-}C_4H_9)_4NCl(\text{ca.}30)H_2O$, was formed. Then, two types of solutions (solutions I and II) were prepared: Solution I was prepared by melting the solid phase at a temperature of only 1° higher than its dissolution temperature; Solution II was prepared by adding urea into solution I at the same temperature. For solutions I and II, the supercooling temperatures at which a hydrate crystal phase appeared when the solution (ca. 5 g) was cooled at a rate of 0.2°C/min in a constant-temperature bath with slight stirring, were measured. In order to compare the behavior of aqueous solutions of tetrabutylammonium salts with those of simple electrolytes, for which the effect due to the formation of hydrogen-bonded water networks

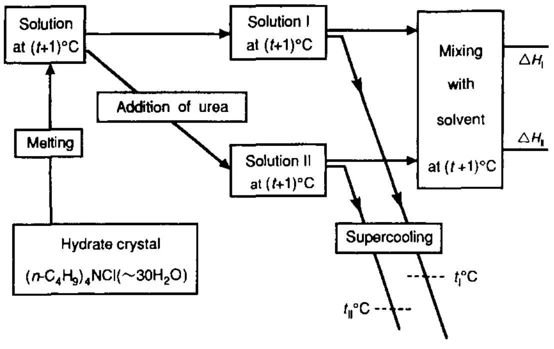

Fig. 1. Schematic presentation for the preparation of solutions I and II for the measurements of supercooling temperature and enthalpy of mixing.

cannot be expected, similar experiments were carried out for KCl and $CaCl_2$ solutions. For both salts, saturated aqueous solutions at 20°C were used.

3. Results and discussion

3.1. Determination of experimental conditions

In order to determine the experimental conditions the solution behavior of the ternary solutions, $(n\text{-}C_4H_9)_4NCl$–urea–H_2O, was examined by solid–liquid phase diagrams and thermal analysis using a differential scanning calorimeter.

The solid–liquid phase diagrams obtained are shown in Fig. 2. The logarithm of the concentration expressed as the mole fraction X is plotted against the reciprocal of the absolute temperature as a function of the molar ratio of $(n\text{-}C_4H_9)_4NCl$ to urea. The mole fraction X denotes the concentration of $(n\text{-}C_4H_9)_4NCl$ in a pseudo binary mixture of $(n\text{-}C_4H_9)_4NCl$ with water. The temperature expressed in ordinary Celsius unit is shown on the upper side of the figure. This phase diagrams clearly indicate the formation of hydrates, $(n\text{-}C_4H_9)_4NCl(ca.30)H_2O$, even in the presence of urea because the concentration at which the formation of the hydrate occur is almost the same (X=0.02) regardless of the amount of urea added. However, the melting point of the hydrate are lowered remarkably by increasing the amount of urea.

Fig. 3 shows some representative DSC signals for aqueous solutions of $(n\text{-}C_4H_9)_4NCl$ with X=0.02 as a function of molar ratio of $(n\text{-}C_4H_9)_4NCl$ to urea. It is

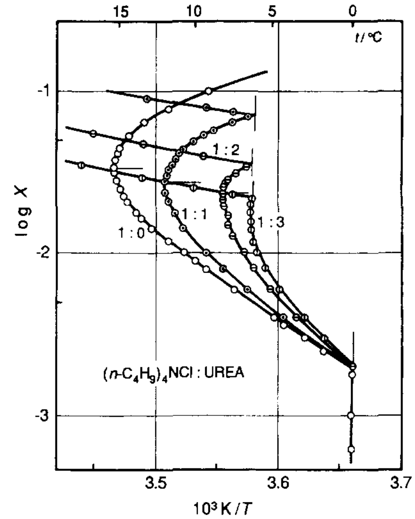

Fig. 2. Solid–liquid phase diagrams for the water–$(n\text{-}C_4H_9)_4NCl$–urea systems.

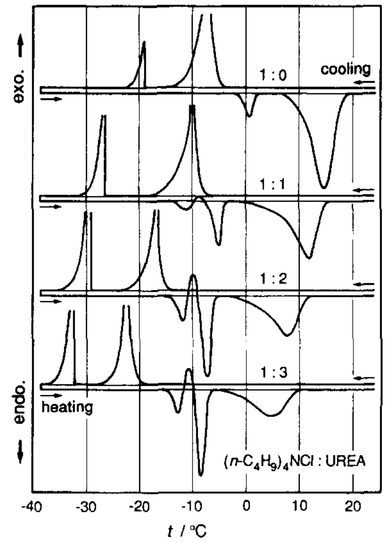

Fig. 3. Temperature dependence of the DSC signals, expressed in an arbitrary unit, for the systems water–$(n\text{-}C_4H_9)_4NCl$–urea.

obvious that both the exothermic peaks around −10 to −20°C and the endothermic peaks around 15 to 5°C indicate the solidification and melting of a hydrate phase. The dissolution temperature of a hydrate approximately coincides with that shown in Fig. 2. The exothermic peaks around −20 to −30°C and the endothermic peaks around 0 to −10°C arise from the solidification and the melting of ice. The exothermic peaks around −10°C in the heating curve seem to be due to the presence of urea.

From both solid–liquid phase diagrams and DSC measurements, it was concluded that (1) urea molecule was not incorporated within the hydrate phase and (2) the appropriate concentrations of $(n\text{-}C_4H_9)_4NCl$ were in the range of X=0.01 to 0.03 if the molar ratio of urea to water was kept at 1 : 49.

3.2. Supercooling temperatures

In Fig. 4, the observed supercooling temperatures for solution II (t_{II} values) are plotted against those for solution I (t_I values) for three tetrabutylammonium chloride solutions together with two simple inorganic salts, KCl and $CaCl_2$. In solution II, the molar ratio of urea to water was 1 : 49. In this figure, the results for aqueous solutions of KCl and $CaCl_2$ fall around the line, which indicates that t_I values are equal to the t_{II} values. This behavior clearly indicates that the solidification process of KCl and $CaCl_2 \cdot 6H_2O$ is not influenced by the addition of urea. However, for tetrabutylammonium chloride solutions, the t_I values are about 20°C higher than the t_{II} values regardless of the concentrations. The same phenomena were also observed for solutions which were thermally destroyed by raising to high temperatures [3] and were destroyed by irradiation with ultrasonic waves [4]. This results presumably suggest that hydrogen-bonded water networks around the butyl chain of the ammonium cation in solution I are much more similar to those in a hydrate crystal than those in solution II: the order of the hydrogen-bonded water networks around butyl groups in solution II are partially destroyed by the presence of urea.

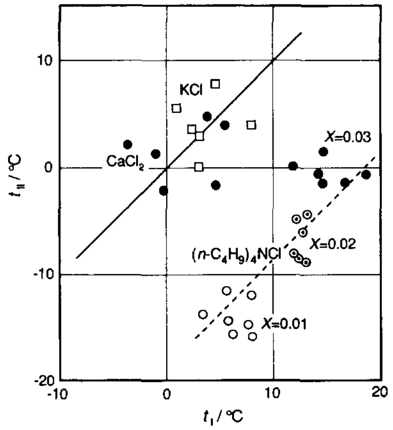

Fig. 4. Relationship between the supercooling temperatures t_I and t_{II} for aqueous solutions of $(n\text{-}C_4H_9)_4NCl$ (X=0.01, 0.02, 0.03), KCl, and $CaCl_2$.

3.3. Enthalpies of mixing

The enthalpy changes when 0.2 g of an aqueous solutions of $(n\text{-}C_4H_9)_4NCl$ with X=0.02 is mixed with 25 ml of three kinds of solvents at 15°C are given in Table 1. The temperature of 15°C corresponds to about 1° higher than the dissolution temperature (13.8°C, Fig. 2) of the $(n\text{-}C_4H_9)_4NCl$ solution with X=0.02. The ΔH_I and ΔH_{II} values indicate the results for solution I ($(n\text{-}C_4H_9)_4NCl : H_2O=1 : 49$) and solution II ($(n\text{-}C_4H_9)NCl : H_2O$: urea : 1 : 49 : 1), respectively. These values are the mean values of ten measurements, and are attached by probable errors. All the values are expressed in kJ/mol of water. Table 1 also includes the differences between ΔH_I and ΔH_{II}, $\Delta H_I - \Delta H_{II}$.

Although each enthalpy of mixing is dependent on the type of solvent, the differences $\Delta H_I - \Delta H_{II}$ are all small and positive, indicating that slightly more heat is necessary when solution I is mixed with a solvent compared to solution II. It is interesting to note that the $\Delta H_I - \Delta H_{II}$ values are nearly equal regardless of the type of solvent. The mean value for three solvents is equal to 0.36 kJ/mol of water. This value seems to reflect the energy difference of hydrogen-bonded water networks around a $(n\text{-}C_4H_9)_4NCl$ molecule between solutions I and II for the following reasons: (1) in the final state of mixing, all the molecules are dispersed monomolecularly because the moral ratios of $(n\text{-}C_4H_9)_4NCl : H_2O$: urea : solvent are equal to

Table 1

Enthalpies of mixing in kJ/mol of water of aqueous $(n\text{-}C_4H_9)_4NCl$ solutions (X=0.02) with various solvents at 15°C

	Solvent		
	Acetone	Tetrahydrofuran	1,4-Dioxane
ΔH_I	4.08±0.03	4.35±0.02	5.53±0.03
ΔH_{II}	3.73±0.02	4.01±0.02	5.15±0.03
$\Delta H_I - \Delta H_{II}$	0.35±0.03	0.34±0.02	0.38±0.03

1 : 49 : 1: ca. 2000, and (2) (n-$C_4H_9)_4NCl$–solvent, water–solvent, and urea–solvent interactions are expected to be relatively weak.

Although the effect of the presence of urea on the ΔH_{II} values cannot exactly be estimated, this effect may not exceed the difference between the enthalpy of mixing of pure water and that of aqueous solution of urea (water : urea=49 : 1). This difference was found to be 0.19±0.03 kJ/mol of water when the solvent was acetone. As a result, it can be concluded that the net value of $\Delta H_I - \Delta H_{II}$ is approximately equal to 0.17 kJ/mol of water if the effect due to the presence of urea is taken into consideration. It is interesting to note that this value is almost the same as those found for the systems whose water structure was destroyed either by heating to 80°C (0.20 kJ/mol of water) [3] or by irradiation with ultrasonic waves (0.18 kJ/mol of water) [4].

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