Supercooling and Enthalpy of Mixing of Aqueous Solutions of Tetrabutyl(or isopentyl)ammonium Chloride Subjected to Irradiation with Ultrasonic Waves

Haruo Nakayama,* Chihiro Hayashi, and Masato Endou

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

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In order to observe more directly the structural organization of water molecules around a nonpolar molecule in an aqueous solution, the supercooling temperatures and enthalpies of mixing with various solvents were measured using two kinds of aqueous solutions (solutions I and II) of tetrabutyl(or isopentyl)ammonium chloride, which were subjected to different treatments. Solution I was made by melting a hydrate solid formed from the ammonium salts and water and by keeping its temperature only one degree Celsius higher than its dissolution temperature; solution II was made by irradiating solution I with ultrasonic waves (38 kHz) for 20 min at the same temperature as solution I. The supercooling temperatures of solution I were found to be about 10 degrees Celsius higher than those of solution II. The differences in the enthalpies of mixing between solution I and solution II in the same solvent, $\Delta H_{\mathrm{I}}-\Delta H_{\mathrm{II}}$, were found to be about 3 kJ per mole of $(n\text{-}C_4H_9)_4NCl$ for most of the solvents. It has been concluded that these results directly reflect the difference in the stability of hydrogen-bonded water networks around either a butyl or an isopentyl chain of the ammonium cation in aqueous solutions.

It is well-known that such tetraalkylammonium salts as tetrabutylammonium chloride ($(n\text{-}C_4H_9)_4NCl$) and tetraisopentylammonium chloride ($(i\text{-}C_5H_{11})_4NCl$) 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 former salt and around 40 for the latter; the melting points are 15.0 and 29.6 °C, respectively[1]). These hydrates may be regarded as being of the same type as those of $(n\text{-}C_4H_9)_4NF$[2] and $(i\text{-}C_5H_{11})_4NF$.[3]

According to a single-crystal X-ray examination by Jeffrey and co-workers,[2,3] these hydrates were of the semi-clathrate type, similar to the so-called gas hydrates:[4] the water structure is a hydrogen-bonded framework, and is essentially a regular arrangement of polyhedra, such as pentagonal dodecahedra and tetrakaidecahedra; each alkyl group of an ammonium cation is incorporated into one of the polyhedra.

In our previous study[5] it was found that the enthalpies of solution in a saturated aqueous solution (ΔH_{sat}) of clathrate-like hydrate solids, such as $(n\text{-}C_4H_9)_4NCl(\text{ca. }30)H_2O$ and $(i\text{-}C_5H_{11})_4NCl(\text{ca. }40)H_2O$, corresponded to about 90% of the enthalpies of fusion of these hydrate solids (ΔH_{f}), and further, that these enthalpies of fusion were approximately equal to the product of the hydration numbers of the hydrates and the molar enthalpy of fusion of ice I. These facts clearly suggest that the state of the hydrogen-bonded water networks around the alkyl chains, like $n\text{-}C_4H_9$ and $i\text{-}C_5H_{11}$ in an aqueous solution, are 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.

Although there is a good deal of evidence that nonpolar molecules, such as hydrocarbon molecules, can increase the structural organization of water[6,7] (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 the solubilities in water, partial molar volumes and heat capacities.

In our previous study,[8] a new attempt was made to observe more directly the stabilities of hydrogen-bonded water networks around nonpolar molecules using aqueous solutions of either $(n\text{-}C_4H_9)_4NCl$ or $(i\text{-}C_5H_{11})_4NCl$; the supercooling temperatures and enthalpies of mixing with various solvents were examined for two kinds of solutions (solutions I and II). The temperature of solution I was kept at only one degree Celsius higher than its dissolution temperature in order to retain as much hydrogen-bonded water structure as possible; that of solution II was raised to 80 °C in order to destroy the water structure thermally. It was found that the supercooling temperatures of solution I were higher than those of solution II, and that the enthalpies of mixing of solution I were more endothermic than those of solution II. These results directly show the difference in the stabilities of the hydrogen-bonded water networks in these two solutions.

In this study similar types of experiments were carried out in order to determine whether such a difference can also be observed for solutions whose water networks had been destroyed by irradiation with ultrasonic waves.

Experimental

An aqueous solution of tetrabutylammonium chloride ($(n\text{-}C_4H_9)_4NCl$) was prepared by the neutralization of a tetrabutylammonium hydroxide solution with hydrochloric acid. The hydroxide solution was obtained by treating tetrabutylammonium iodide with freshly prepared silver(I) oxide in water, followed by filtration of the resulting silver iodide in a CO_2-free atmosphere. Tetrabutylammonium iodide was prepared by precipitation from an aqueous solution of tetrabutylammonium bromide (purchased from Tokyo Kasei Kogyo Co., Ltd.) with the addition of sodium iodide, followed by washing with water and air-drying in a desiccator. The iodide was purified by repeated recrystallization from ethyl acetate.

An aqueous solution of tetraisopentylammonium chloride ($(i\text{-}C_5H_{11})_4NCl$) was prepared in a similar way as the $(n\text{-}C_4H_9)_4NCl$ solution mentioned above. Tetraisopentylammonium iodide was synthesized by reacting triisopentylamine with isopentyl iodide in ethyl acetate, and subsequently purified by repeated recrystallization from an ethyl acetate–acetone mixture. 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(hydrate)–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 experiments,[8] six solutions were chosen as being appropriate for carrying out the experiments. These solutions are listed in Table 1 together with the dissolution temperatures at which the hydrate solid phase completely disappeared when the hydrate solid–aqueous solution equilibrium mixtures were 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 $(n\text{-}C_4H_9)_4NCl(\text{ca. }30)H_2O$ or $(i\text{-}C_5H_{11})_4NCl(\text{ca. }40)H_2O$, was formed. Then, two types of solutions (solutions I and II) were prepared: Solution I was prepared by melting the hydrate crystal at a temperature only one degree Celsius higher than its dissolution temperature (listed in Table 1); solution II was prepared by irradiating solution I with ultrasonic waves (38 kHz) for 20 min at the same temperature as solution I.

Table 1. Mole Fractions X and the Dissolution Temperatures t of the Aqueous Solutions Used in These Experiments

Salt	X	t/°C
$(n\text{-}C_4H_9)_4NCl$	0.01	10.3
	0.02	13.8
	0.03	14.5
$(i\text{-}C_5H_{11})_4NCl$	0.001	19.1
	0.003	23.9
	0.006	26.4

For solutions I and II, the supercooling temperatures at which a hydrate crystal phase appeared when the solution (about 5 g) was cooled at a rate of 0.2 °C per minute in a constant-temperature bath with slight stirring, were measured. Furthermore, for solutions I and II of $(n\text{-}C_4H_9)_4NCl$ with $X=0.02$, measurements of the enthalpy of mixing with various solvents (water, methanol, ethanol, acetone, tetrahydrofuran, and 1,4-dioxane) at 15 °C (which were about one degree Celsius higher than the dissolution temperature of 13.8 °C, Table 1), were also made. The calorimeter used was a twin-type conduction calorimeter manufactured by Tokyo Riko (TCC-21). About 0.2 g of each solution, which had been sealed in a glass ampoule, was mixed with 25 ml of the solvents. An ampoule containing 0.2 g of the solvent was used as a reference. These experimental procedures are illustrated in Fig. 1.

In order to compare the behavior of aqueous solutions of tetraalkylammonium salts with those of simple electrolytes, for which the effect due to the formation of hydrogen-bonded water networks 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. Solution I was made by keeping the solution at 21 °C and solution II by irradiating solution I with ultrasonic waves (38 kHz) for 20 min at 21 °C. Although $CaCl_2$ forms a hydrate ($CaCl_2 \cdot 6H_2O$) at room temperature, the water structure in the hydrate solid is quite different from that in the tetraalkylammonium salt hydrate mentioned above.

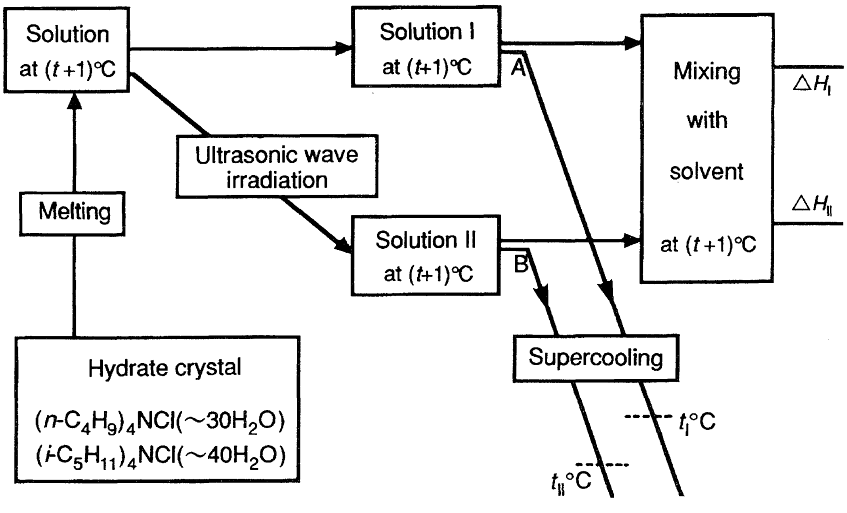

Fig. 1. Schematic presentation for the preparation of solutions I and II and for the measurements of supercooling temperature and enthalpy of mixing.

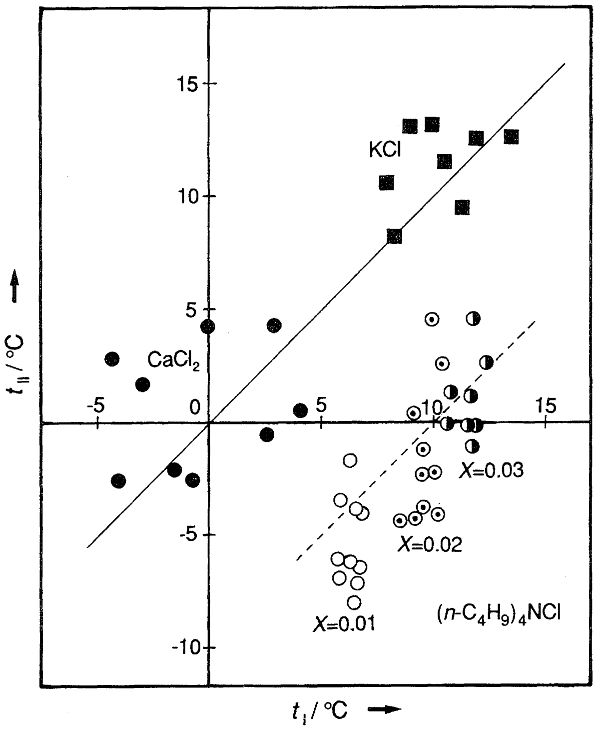

Fig. 2. Relationship between the supercooling temperatures t_I and t_{II} for aqueous solutions of $(n\text{-}C_4H_9)_4NCl$ ($X = 0.01$, 0.02, 0.03), KCl, and $CaCl_2$.

Results and Discussion

Supercooling. In Fig. 2 the observed supercooling temperatures for solution II (t_{II} values) are plotted against those for the solution I (t_I values) for three tetrabutylammonium chloride solutions (listed in Table 1) together with two simple inorganic salts, KCl and $CaCl_2$. Similar data for the three tetraisopentylammonium chloride solutions (listed in Table 1) are shown in Fig. 3. In these figures, the results for aqueous solutions of KCl and $CaCl_2$ fall around the line, which indicates that the t_I values are equal to the t_{II} values. This behavior clearly indicates that the state of water molecules is not affected by the irradiation of ultrasonic waves, as expected. However, for both tetrabutylammonium chloride solutions (Fig. 2) and tetraisopentylammonium chloride solutions (Fig. 3), the t_I values are higher than the t_{II} values: The t_I values are about 10 °C higher than the t_{II} values for the $(n\text{-}C_4H_9)_4NCl$ solutions and about 12 °C for the $(i\text{-}C_5H_{11})_4NCl$ solutions regardless of their concentrations. These results presumably suggest that hydrogen-bonded water networks around the alkyl chain (either butyl chain or isopentyl 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 alkyl groups in solution II are partially destroyed by irradiation with ultrasonic wave. The results shown in Figs. 2 and 3 also indicate that temperatures t_{II} are widely distributed compared with temperatures t_I. This behavior suggests that the effect of irradiation with ultrasonic waves on the structure of water is not necessarily the same for each experiment.

It is interesting to note that points A and B in Fig. 1 have the same thermodynamic variables as well as the same temperature, pressure, and concentration. Therefore, the cooling processes for solutions I and II are the same. In spite of this, the experimental fact that the t_I values are different from the t_{II} values clearly indicates that mechanically destroyed hydrogen-bonded water networks around the alkyl group in solution II cannot easily revert to a state in solution I within the time interval examined. The same phenomena were also observed for solutions which were thermally destroyed by raising the temperature.[8]

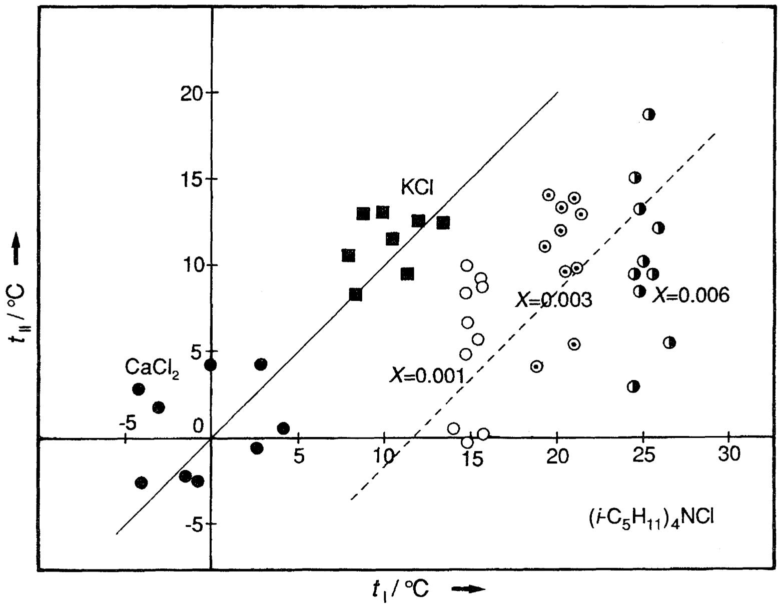

Fig. 3. Relationship between the supercooling temperatures t_I and t_{II} for aqueous solutions of $(i\text{-}C_5H_{11})_4NCl$ ($X = 0.001$, 0.003, 0.006), KCl, and $CaCl_2$.

Table 2. Enthalpies of Mixing in kJ mol^{-1} of Aqueous $(n\text{-}C_4H_9)_4NCl$ Solutions ($X=0.02$) with Various Solvents at 15 °C

	Solvent					
	Acetone	Tetrahydrofuran	1,4-Dioxane	Ethanol	Methanol	Water
ΔH_{I}	200 ± 1	213 ± 1	271 ± 1	-77.2 ± 0.5	-127 ± 1	-13.3 ± 0.1
ΔH_{II}	197 ± 1	210 ± 1	267 ± 1	-79.5 ± 0.3	-130 ± 1	-13.6 ± 0.1
$\Delta H_{\mathrm{I}}-\Delta H_{\mathrm{II}}$	3 ± 1	3 ± 1	4 ± 1	2.3 ± 0.5	3 ± 1	0.3 ± 0.2

Enthalpies of Mixing. In order to compare the energetic stabilities of the water networks around the tetrabutylammonium ion between solution I and solution II, the enthalpies of mixing of these two types of solutions with various solvents were measured. The enthalpy changes when 0.2 g of an aqueous solution of $(n\text{-}C_4H_9)_4NCl$ with $X=0.02$ (23.9 wt%) is mixed with 25 ml of various types of solvents at 15 °C are given in Table 2. The temperature of 15 °C corresponds to about one degree Celsius higher than the dissolution temperature (13.8 °C, Table 1) of the $(n\text{-}C_4H_9)_4NCl$ solution with $X=0.02$. The ΔH_{I} and ΔH_{II} values indicate the results for solutions I and II, respectively. These values are the mean values of ten measurements, and are attached by probable errors. All of the values are expressed in kJ per mole of $(n\text{-}C_4H_9)_4NCl$. Table 2 also includes the differences between ΔH_{I} and ΔH_{II}, $\Delta H_{\mathrm{I}}-\Delta H_{\mathrm{II}}$.

Both ΔH_{I} and ΔH_{II} have fairly large positive values in such solvents as acetone, tetrahydrofuran, and 1,4-dioxane, and have large negative values in methanol and ethanol. These values are essentially determined by the enthalpy of mixing of each solvent with water which is contained in the sample solution.

Although each enthalpy of mixing is dependent on the type of solvent, the differences $(\Delta H_{\mathrm{I}}-\Delta H_{\mathrm{II}})$ are all small and positive, indicating that slightly more heat is necessary when solution I is mixed with a solvent compared to solution II, regardless of the type of solvent. It is interesting to note that for five solvents, except for water, the $\Delta H_{\mathrm{I}}-\Delta H_{\mathrm{II}}$ values are nearly equal to 3 kJ mol^{-1}. This value seems to represent the energy difference of hydrogen-bonded water networks around one mole of $(n\text{-}C_4H_9)_4NCl$ molecules between solutions I and II for the following reasons. In the final states of mixing of aqueous solutions of $(n\text{-}C_4H_9)_4NCl$ with these solvents both water and $(n\text{-}C_4H_9)_4NCl$ molecules may be dispersed monomolecularly, because: (1) the molar ratios of $(n\text{-}C_4H_9)_4NCl$: water : solvent are equal to 1 : 49 : about 2000, and (2) $(n\text{-}C_4H_9)_4NCl$–solvent interaction is expected to be relatively weak. Since the mole fraction of the $(n\text{-}C_4H_9)_4NCl$ solution is 0.02, the value of 3 kJ per mole of $(n\text{-}C_4H_9)_4NCl$ corresponds to about 0.061 kJ per mole of water, which is about 1.0% of the heat of fusion of ice I. Although this value cannot be discussed in detail at present, it is important to note that information about the stability of hydrogen-bonded water networks around a nonpolar molecule can be more directly obtained by such experiments.

As reported earlier,[8] for solutions II, whose water structure was destroyed by heating to 80 °C, the differences $(\Delta H_{\mathrm{I}}-\Delta H_{\mathrm{II}})$ were about three-times larger than those observed in this experiment. This fact simply suggests that the effective power of destroying the water networks around the butyl chain of the $(n\text{-}C_4H_9)_4NCl$ molecule is fairly different between raising the temperature to 80 °C and irradiation with ultrasonic waves (38 kHz, 20 min) in this experiment.

The mixing processes of solutions I and II with water are essentially different from those with other solvents; the hydrogen-bonded water networks around the alkyl chain become more stable owing to the increased amount of water molecules participating in the formation of networks. In spite of this, if the final states attained by the mixing process with water are the same for both solutions I and II, the $\Delta H_{\mathrm{I}}-\Delta H_{\mathrm{II}}$ value should be independent of the kinds of solvent, since both ΔH_{I} and ΔH_{II} simply indicate the difference of enthalpy between an initial state and a final state.

However, as shown in Table 2, when the solvent is water the difference $(\Delta H_{\mathrm{I}}-\Delta H_{\mathrm{II}})$ is fairly small (0.3 kJ mol^{-1}) compared with those for the other solvents (3 kJ mol^{-1}). This fact indicates that the final states attained by the mixing process with water are still different for solutions I and II. Both states seem to be non-equilibrium states, just as shown for states A and B in Fig. 1.

References

1) H. Nakayama, *Bull. Chem. Soc. Jpn.*, **54**, 3717 (1981).

2) R. K. McMullan, M. Bonamico, and G. A. Jeffrey, *J. Chem. Phys.*, **39**, 3295 (1963).

3) D. Feil and G. A. Jeffrey, *J. Chem. Phys.*, **35**, 1863 (1961).

4) W. F. Clausen, *J. Chem. Phys.*, **19**, 259, 662 (1951); L. Pauling and R. E. Marsh, *Proc. Natl. Acad. Sci. U.S.A.*, **38**, 112 (1952).

5) H. Nakayama, *Bull. Chem. Soc. Jpn.*, **55**, 389 (1982).

6) W.-Y. Wen, in "Water and Aqueous Solutions," ed by R. A. Horn, Wiley-Interscience, New York (1972), Chap. 15, p. 613.

7) I. M. Klotz, in "Horizons in Biochemistry," ed by M. Kasha and B. Pullman, Academic Press, New York (1962), p. 523.

8) H. Nakayama and C. Hayashi, *Thermophimica Acta*, **253**, 77 (1995).