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Thermochimica Acta 253 (1995) 77–84

thermochimica
acta

Supercooling and enthalpy of mixing of aqueous solutions of tetrabutylammonium (or isopentylammonium) chloride subjected to different thermal treatments ☆

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Received 7 June 1994; accepted 1 July 1994

Abstract

In order to observe more directly the structural organization of water molecules around an apolar molecule in an aqueous solution, supercooling phenomena and enthalpies of mixing with various solvents have been examined using aqueous solutions of tetrabutylammonium (or isopentylammonium) chloride subjected to different thermal treatments. Solution I was kept at a temperature only one degree higher than its dissolution temperature, at which a hydrate crystal phase was completely dissolved. The temperature of solution II was raised to 80°C. The supercooling temperatures of solution I were found to be rather higher than those of solution II: 10–15°C for $(n\text{-}C_4H_9)_4NCl$ and about 20°C for $(\text{i-}C_5H_{11})_4NCl$, regardless of the concentrations of these salts. The differences of the enthalpies of mixing between solution I and solution II in the same solvent $\Delta H_I - \Delta H_{II}$ were determined. It was found that, (1) for solvents such as acetone, tetrahydrofuran, and 1,4-dioxane, $\Delta H_I - \Delta H_{II}$ values were about 10 kJ per mole of $(n\text{-}C_4H_9)_4NCl$ which contained 49 moles of water (i.e. the mole fraction of a sample solution was 0.02), and (2) when the solvents were alcohols (methanol and ethanol), the $\Delta H_I - \Delta H_{II}$ value became rather small and in the case of water the $\Delta H_I - \Delta H_{II}$ value became even smaller (1.1 kJ mol^{-1}). It is concluded that the difference in the stability of water networks between solutions I and II is 0.204 kJ per mole of water, which corresponds to about 3.4% of the enthalpy of fusion of ice I.

Keywords: Heat of mixing; Isopentylammonium chloride; Phase diagram; SLE; Supercooling; Tetrabutylammonium chloride

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☆ Paper presented at the International and III Sino–Japanese Symposium on Thermal Measurements, Xi'an, 4–6 June 1994.

SSDI 0040-6031(94)02017-5

1. Introduction

There is a good deal of evidence that various apolar molecules, such as hydrocarbon molecules, can increase the structural organization of water [1,2]. In many cases, however, this organizing ability of an apolar substance on water molecules has been discussed on the basis of indirect information such as temperature dependence of the solubilities, partial molar volumes, enthalpies of solution (or transfer), heat capacities, activity and osmotic coefficients. In this study, a new attempt has been made to investigate more directly the properties of hydrogen-bonded water networks around apolar molecules using tetraalkylammonium salt solutions which were subjected to different thermal treatments. The tetraalkylammonium salts used were tetrabutylammonium chloride ($(n\text{-}C_4H_9)_4NCl$) and tetraisopentylammonium chloride ($(i\text{-}C_5H_{11})_4NCl$). These two salts can form unusual hydrates which have a large number of water molecules per ammonium ion (hydration numbers) (around 30 for the former salt and around 40 for the latter [3]), and fairly high melting points (15.0 and 29.6°C, respectively [3]). These hydrates may be regarded as the same type as the hydrates of $(n\text{-}C_4H_9)_4NF$ [4] and $(i\text{-}C_5H_{11})_4NF$ [5]. According to a single-crystal X-ray examination by Jeffrey and co-workers [4,5] these hydrates were semi-clathrate hydrates, similar to the so-called gas hydrates [6]: 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.

However, in our previous study [7] it was found that the enthalpies of solution in a saturated aqueous solution (ΔH_{sat}) of clathrate-like hydrate solids such as $(n\text{-}C_4H_9)_4NCl(\approx 30)H_2O$ and $(i\text{-}C_5H_{11})_4NCl(\approx 40)H_2O$ correspond to about 90% of enthalpies of fusion of these hydrate solids (ΔH_f), and further that these enthalpies of fusion are approximately equal to the product of the hydration numbers of the hydrates and molar enthalpy of fusion of ice I. These facts suggest that the state of hydrogen-bonded water networks around the $n\text{-}C_4H_9$ group in an aqueous solution of $(n\text{-}C_4H_9)_4NCl$ is essentially similar to that in the melt of the $(n\text{-}C_4H_9)_4NCl$ hydrate. A similar argument can be applied to the $(i\text{-}C_5H_{11})_4NCl$ hydrate. In conclusion, a stable hydrogen-bonded water structure around the alkyl chain in the hydrate solid remains in its aqueous solution to a great extent.

In this study the difference in the stabilities of hydrogen-bonded water networks in two kinds of aqueous solutions (solutions I and II), of either $(n\text{-}C_4H_9)_4NCl$ or $(i\text{-}C_5H_{11})_4NCl$ is discussed by examining supercooling phenomena and enthalpies of mixing with various solvents. Solution I was kept at a temperature only one degree higher than its dissolution temperature in order to retain as much water stability as possible and the temperature of solution II was raised to 80°C in order to destroy the water structure. For comparison, the behaviors of aqueous solutions of simple inorganic salts (KCl and $CaCl_2$) were also examined.

2. Experimental

An aqueous solution of tetraisopentylammonium chloride ($(i\text{-}C_5H_{11})_4NCl$) was prepared by neutralization of tetraisopentylammonium hydroxide solution with hydrochloric acid. The hydroxide solution was obtained by treating tetraisopentylammonium iodide with freshly prepared silver(I) oxide in water followed by filtration of the resulting silver iodide in a CO_2-free atmosphere.

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.

An aqueous solution of tetrabutylammonium chloride ($(n\text{-}C_4H_9)_4NCl$) was prepared in a similar way as the $(i\text{-}C_5H_{11})_4NCl$ solution mentioned above.

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.

In order to determine the concentrations of the solutions which were appropriate for carrying out the experiments, the hydrate solid–liquid phase diagrams of the binary systems of $(n\text{-}C_4H_9)_4NCl\text{–}H_2O$ and $(i\text{-}C_5H_{11})_4NCl\text{–}H_2O$ were first examined in the following manner. A sample solution (about 1.0 g) of known concentration 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 corresponding ammonium ion with a 0.02 mol dm^{-3} sodium tetraphenylborate solution, which had been standardized with a known amount of pure $(n\text{-}C_4H_9)_4NI$. Each ampoule was gradually cooled until the solid phase appeared and was annealed for at least 24 h at a temperature a few degrees lower than the temperature at which the solid phase dissolved completely. After that, the ampoule was slowly warmed, at a rate of about 0.5 K h^{-1}, with vigorous shaking in a constant-temperature bath; the temperature at which the solid phase disappeared completely was accurately determined. The hydrate solid–liquid phase diagrams obtained are shown in Fig. 1. The logarithm of the concentration expressed as the mole fraction X is plotted against the reciprocal of the absolute temperature. The temperature expressed in ordinary Celsius units is shown on the upper side of the figure. The phase diagrams shown in Fig. 1 clearly indicate the formation of hydrates which have large hydration numbers and fairly high melting points: $(n\text{-}C_4H_9)_4NCl(\approx 30)H_2O$ and $(i\text{-}C_5H_{11})_4NCl(\approx 40)H_2O$. On the basis of these phase diagrams, six solutions were chosen as sample solutions. Their concentrations are shown in Fig. 1 and listed in Table 1 together with the dissolution temperatures.

To each solution listed in Table 1 the following procedures were applied. By repeated cooling and heating of the solution well-formed hydrate crystal (either $(n\text{-}C_4H_9)_4NCl(\approx 30)H_2O$ or $(i\text{-}C_5H_{11})_4NCl(\approx 40)H_2O$) was formed. Then two types of solution, which were subjected to different thermal histories, were obtained: solution I was prepared by melting the hydrate crystal at a temperature only one

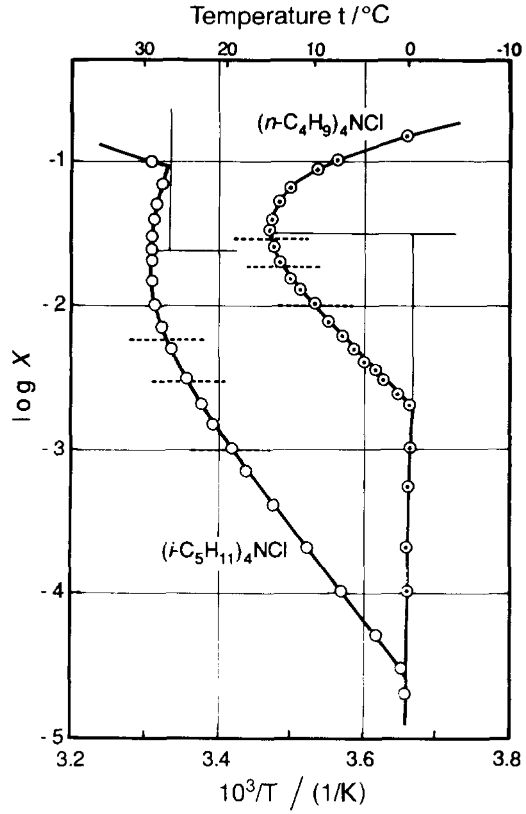

Fig. 1. Solid–liquid phase diagrams for the water–$(n\text{-}C_4H_9)_4NCl$ and water–$(i\text{-}C_5H_{11})_4NCl$ systems.

degree higher than its dissolution temperature (listed in Table 1) and solution II by melting the hydrate crystal at 80°C, which is a fairly high temperature compared with its dissolution temperature.

For solutions I and II supercooling temperatures, at which a hydrate crystal phase appeared when a solution (about 5 g) was cooled at a rate of 0.2 K min^{-1} 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 enthalpy of

Table 1
Mole fractions X and dissolution temperatures t of the aqueous solutions used in these experiments

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

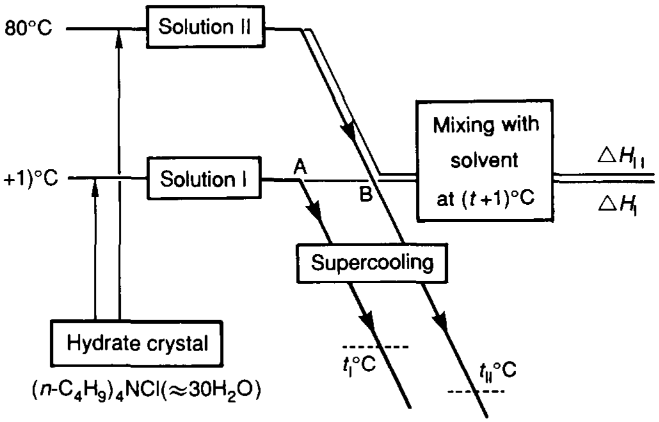

Fig. 2. Schematic presentation for the preparation of solutions I and II and for the measurements of supercooling temperature and enthalpy of mixing.

mixing with water, methanol, ethanol, acetone, tetrahydrofuran, and 1,4-dioxane at 15°C (which was about one degree higher than the dissolution temperature of 13.8°C) 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 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. These experimental procedures are illustrated in Fig. 2.

In order to compare the behavior of tetraalkylammonium salts with those of simple electrolytes, similar experiments were carried out for KCl and $CaCl_2$ solutions. Although the latter salt forms a hydrate ($CaCl_2 \cdot 6H_2O$) at room temperature, the water structure in a hydrate solid is different from that in the tetraalkylammonium salt hydrate mentioned above. For both salts, saturated solutions at 20°C were used: solution I was kept at 21°C and the temperature of solution II was raised to 80°C.

3. Results and discussion

3.1. Supercooling

In Fig. 3 the observed supercooling temperatures for solution II (t_{II} values) are plotted against those for solution I (t_I values), for the six tetraalkylammonium salt solutions listed in Table 1 and two simple inorganic salt solutions, KCl and $CaCl_2$. Fig. 3 clearly shows that, for the six ammonium salt solutions, the t_I values are rather higher than the t_{II} values regardless of the type of tetraalkylammonium cation or their concentrations. Roughly speaking the t_I values are 10–15°C higher than the t_{II} values for $(n\text{-}C_4H_9)_4NCl$ solutions, and about 20°C higher for the $(i\text{-}C_5H_{11})_4NCl$ solutions. These results presumably suggest that hydrogen-bonded

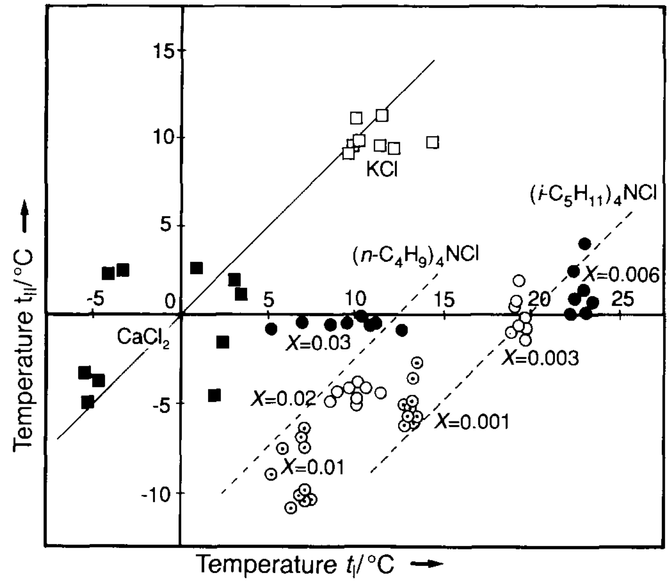

Fig. 3. Relationship between the supercooling temperatures t_I and t_{II} for aqueous solutions of $(n\text{-}C_4H_9)_4NCl$ ($X = 0.01$, 0.02, 0.03), $(i\text{-}C_5H_{11})_4NCl$ ($X = 0.001$, 0.003, 0.006), KCl and $CaCl_2$.

water networks around the alkyl chain of the ammonium cation in solution I are much more similar to those in a hydrate crystal than those in solution II: hydrogen-bonded water networks around alkyl groups in solution II are partially destroyed by raising the temperature. However, it is interesting to note that the points A and B in Fig. 2 have the same thermodynamic variables, the same temperature, pressure, and concentration. Therefore, the cooling processes for solution I from point A and for solution II from point B are the same procedures. In spite of this, the experimental fact that t_I values are different from t_{II} values clearly indicates that thermally 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. It would be reasonable to assume that not only state B but also state A are non-equilibrium states to which the usual thermodynamics cannot be applied. In Fig. 3, the results for aqueous solutions of KCl and $CaCl_2$ fall around the line which indicates that t_I values are equal to t_{II} values, showing that the states of the water molecules are not different in solutions I and II. Thus, the notable difference between the t_I values and t_{II} values in the tetraalkylammonium salt solutions is clearly due to the formation of hydrogen-bonded water networks around alkyl chains such as $n\text{-}C_4H_9$ and $i\text{-}C_5H_{11}$.

3.2. Enthalpies of mixing

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 solvent at 15°C are

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					
	Water	Methanol	Ethanol	Acetone	Tetrahydrofuran	1,4-Dioxane
ΔH_I	-13.3 ± 0.1	-127 ± 1	-77.2 ± 0.5	200 ± 1	213 ± 1	271 ± 1
ΔH_{II}	-14.4 ± 0.2	-130 ± 1	-82.0 ± 0.3	188 ± 1	204 ± 1	261 ± 1
$\Delta H_I - \Delta H_{II}$	1.1 ± 0.2	3 ± 1	4.8 ± 0.6	12 ± 1	9 ± 1	10 ± 1

shown in Table 2. The ΔH_I and ΔH_{II} values indicate the results for solutions I and II, respectively. All 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}, $\Delta H_I - \Delta H_{II}$. Both ΔH_I and ΔH_{II} are dependent on the type of solvent used: they are relatively small, negative (exothermic) values in water and are large, negative (exothermic) values in alcohols and are fairly large, positive (endothermic) values in acetone, tetrahydrofuran, and 1,4-dioxane. These values are essentially determined by the enthalpy of mixing of each solvent with water which is contained in a sample solution.

Although the differences $\Delta H_I - \Delta H_{II}$ are dependent on the type of solvent, they are all small positive values, 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 solvents such as acetone, tetrahydrofuran, and 1,4-dioxane, the $\Delta H_I - \Delta H_{II}$ values are nearly equal to 10 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 the aqueous solutions of $(n\text{-}C_4H_9)_4NCl$ with these solvents, both water molecule and $(n\text{-}C_4H_9)_4NCl$ molecule may be dispersed monomolecularly because, (1) the molar ratios of $(n\text{-}C_4H_9)_4NCl$:water:solvent are roughly equal to $1:49:\approx 2000$, and (2) both $(n\text{-}C_4H_9)_4NCl$–solvent and water–solvent interactions are expected to be relatively weak. The value of 10 kJ per mole of $(n\text{-}C_4H_9)_4NCl$ corresponds to about 0.204 kJ per mole of water, which is about 3.4% of the heat of fusion of ice I. Although this value cannot be discussed in detail at present, it is important to note that energetic information about the hydrogen-bonded water networks around an apolar molecule has actually been obtained.

When the solvents are alcohols (methanol and ethanol) the values of $\Delta H_I - \Delta H_{II}$ are somewhat smaller than those in the above mentioned solvents. Although the reason for these results is not clear at present, it may be considered that specific interactions, especially between water and alcohols, affect the organization of hydrogen-bonded water networks around the $n\text{-}C_4H_9$ chain of the ammonium cation.

The mixing processes of solutions I and II with water are essentially different from those with the other solvents mentioned above because the amount of water molecules participating in the formation of hydrogen-bonded networks around the alkyl chain will be increased by the mixing process. The fact that both ΔH_{I} and ΔH_{II} are negative values indicates that the hydrogen-bonded water networks around the alkyl chain become more stable due to the mixing process with water. It is interesting to note, however, that the difference $\Delta H_{\mathrm{I}} - \Delta H_{\mathrm{II}}$ is small (1.1 kJ mol^{-1}) compared with about 10 kJ mol^{-1} for solvents such as acetone, tetrahydrofuran, and 1,4-dioxane. This behavior may be explained by assuming that the final states attained by the mixing process with water are different for solutions I and II. Both states seem to be non-equilibrium states, just as is found for the states A and B in Fig. 2.

Finally, the experimental fact should be pointed out that no difference between solutions I and II can be found by viscosity measurements, for the following reason: viscosity, which is one of the typical macroscopic properties, reflects a hardness or ease when a solution flows as a whole and is, therefore, not a sensitive property which reflects molecular organization in microscopic regions in the solution.

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