Journal of Thermal Analysis, Vol. 49 (1997) 581-588

Organic Compounds

DIRECT OBSERVATION OF HYDROPHOBIC INTERACTIONS IN AQUEOUS SOLUTIONS OF ORGANIC COMPOUNDS BY SUPERCOOLING AND ENTHALPIES OF MIXING

H. Nakayama and S. Kihara

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

Abstract

Supercooling temperatures and enthalpies of mixing with some solvents have been examined for two kinds of solutions subjected to different thermal treatments (solutions I and II) of tetrahydrofuran (THF), isopropyl alcohol (2-PrOH), and ethyleneglycol butylether (BE), and ethylene- glycol isobutylether (*i*-BE) in order to observe more directly the structural organization of water molecules around a nonpolar molecule in an aqueous solution. For THF and 2-PrOH solutions, supercooling temperatures of solution I were found to be 2–3 degrees higher than those of solution II, and differences ΔH_I–ΔH_{II} were found to be about 3 kJ mol^{-1}. It has been concluded that these results directly reflect the difference in the stability of hydrogen-bonded water networks in an aqueous solution.

Keywords: enthalpy of mixing, hydrophobic hydration, isopropyl alcohol, supercooling temperature, tetrahydrofuran

Introduction

There is a good deal of evidence that nonpolar molecules, such as hydrocarbon molecules, can increase the structural organization of water in aqueous solutions (hydrophobic hydration) [1, 2]. However, this organizing ability of a nonpolar substance has been discussed on the basis of indirect, thermodynamic informations, such as the temperature dependence of solubilities in water, partial molar volumes and heat capacities.

In our previous study [3, 4], a new attempt was made to observe more directly the stabilities of hydrogen-bonded water networks around nonpolar molecules using aqueous solutions of $(n\text{-}C_4H_9)_4NCl$ and $(i\text{-}C_5H_{11})_4NCl$, which are known to form

0368–4466/97/ $ 5.00

John Wiley & Sons Limited
Chichester

clathrate-like hydrates having large hydration numbers [5, 6]; the supercooling temperatures and enthalpies of mixing with various solvents were examined for two kinds of solutions (solutions I and II). The solution I was made by keeping its temperature at only one degree higher than its dissolution temperature in order to retain as much hydrogen-bonded water structure as possible; solution II was made either by heating solution I to 80°C in order to destroy the water structure thermally or by irradiating solution I with ultrasonic waves in order to destroy the water structure mechanically. In these systems 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. It was concluded that these results directly show the difference in the stabilities of the hydrogen-bonded water networks in solutions I and II.

In this study similar types of experiments were carried out in order to determine whether such a difference can also be observed for aqueous solutions of other kind of organic molecules, such as tetrahydrofuran, isopropyl alcohol, and ethyleneglycol monobutylether, in which the growth of hydrogen-bonded water networks is expected to be more weak than that in aqueous solutions of $(n\text{-}C_4H_9)_4NCl$ and $(i\text{-}C_5H_{11})_4NCl$. Tetrahydrofuran was chosen as a simple organic molecule which can form a hydrate at low temperatures [7, 8], isopropyl alcohol and ethyleneglycol butylether as organic molecules which are not known to form any solid phase other than ice at low temperatures. Furthermore, in an aqueous solution of ethyleneglycol butylether, solution II was made by destroying water structure by a liquid-liquid phase separation process.

Experimental

In order to determine the concentrations of the solutions which were appropriate for carrying out the experiments, phase diagrams of the binary systems of tetrahydrofuran–water, isopropyl alcohol–water, ethyleneglycol butylether–water, and ethyleneglycol isobutylether–water were first examined in the following manner. Hereafter we abbreviate tetrahydrofuran to THF, isopropyl alcohol to 2-PrOH, ethyleneglycol butylether (butoxyethanol) to BE, and ethyleneglycol isobutylether to *i*-BE. A sample solution (about 1 g) of known concentration was prepared by weighing out water and each organic liquid; it was then sealed in a small glass ampoule. For the THF–H_2O and 2-PrOH–H_2O systems each ampoule was gradually cooled until the solid phase appeared. After that, the ampoule was slowly warmed, at a rate of about 3 K h^{-1}, with vigorous shaking in a constant temperature bath; the temperature at which the solid phase disappeared completely was accurately determined. For the BE–H_2O and *i*-BE–H_2O systems each ampoule, which was prepared in a similar manner as mentioned above, was slowly heated, at a rate of about 5 K h^{-1}; the temperature at which the solution was separated into two liquid phases was accurately determined. The phase diagrams obtained are shown in Figs 1 and 2. These phase diagrams clearly indicate that (1) THF forms hydrate, THF·$17H_2O$, whose melting point is about 5.1°C; (2) in the 2-PrOH–H_2O binary system the formation of a solid phase other than ice cannot be observed; and (3) in the BE–H_2O

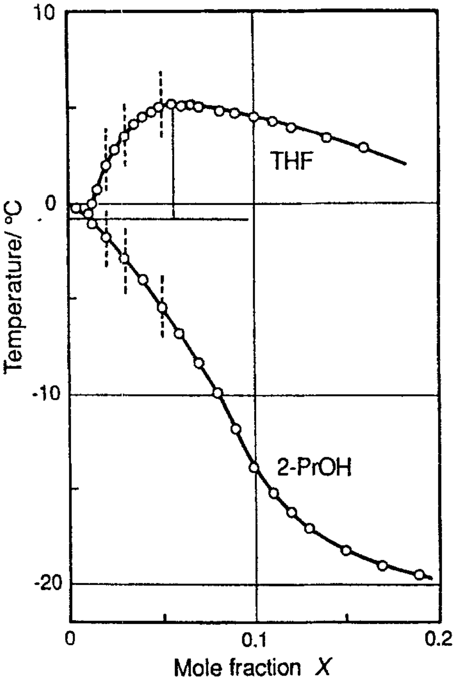

Fig. 1 Solid–liquid phase diagrams for the water–tetrahydrofuran (THF) and water–isopropyl-alcohol (2-PrOH) systems

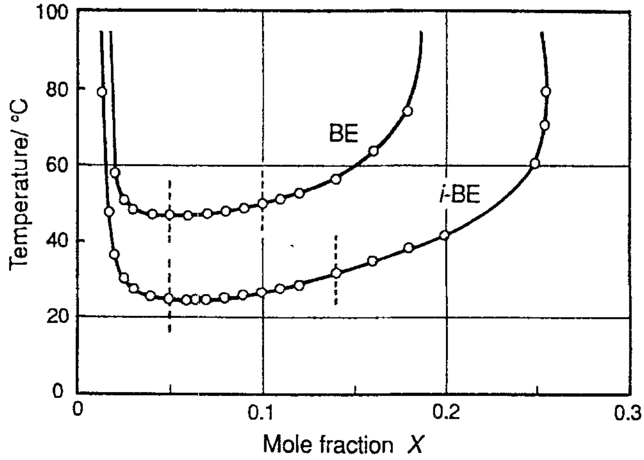

Fig. 2 Liquid–liquid phase diagrams for the water–ethyleneglycol monobutylether (BE) and water–ethyleneglycol isobutylether (*i*-BE) systems

and *i*-BE–H_2O systems the separation into two liquid phases occurs above 47.2 and 25.5°C, respectively. On the basis of these phase diagrams, ten solutions were cho-

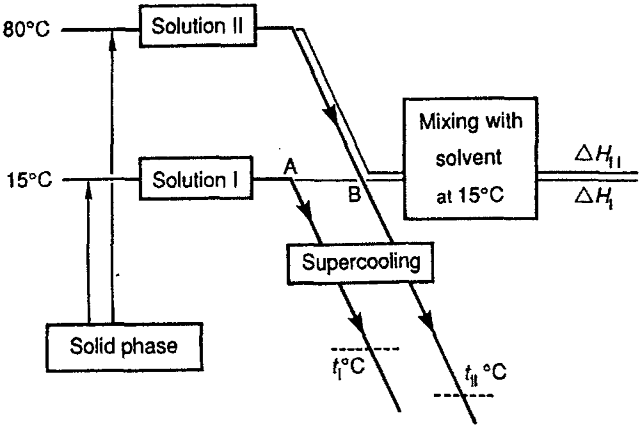

Fig. 3 Schematic presentation for the preparation of solutions I and II and for the measurements of supercooling temperature and enthalpies of mixing

sen as sample solutions. Their concentrations are shown by dotted lines in these phase diagrams.

To each solution the following procedures were applied. A solid phase was obtained by cooling the solution. Then two types of solution, which were subjected to different thermal histories, were obtained: solution I was prepared by melting the solid phase at 15°C and solution II by melting the solid phase at 80°C and kept at that temperature for one hour. For solutions I and II supercooling temperatures, at which a solid phase appeared when a solution 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 THF, 2-PrOH, BE, and *i*-BE with mole fraction of 0.05, measurements of enthalpy of mixing with acetone, THF, and water at 15°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.3.

Results and discussion

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 THF solutions. Similar data for the 2-PrOH solutions (X=0.02 and 0.05), BE solution (X=0.10), and *i*-BE solution (X=0.14) are shown in Fig.5. X denotes the mole fraction of each solute. In these figures, for both THF solutions and 2-PrOH solutions, the t_I values are somewhat higher than the t_{II} values: The t_I values are about 3°C higher than the t_{II} values for the THF solutions and about 2°C for the 2-PrOH solutions regardless of their concentrations. These results presumably suggest that hydrogen-bonded water net-

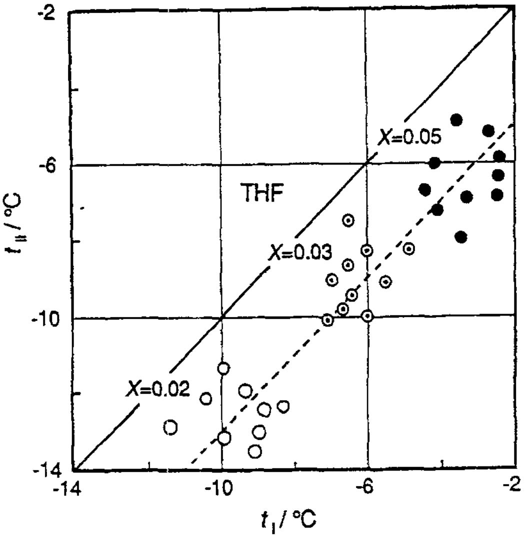

Fig. 4 Relationship between the supercooling temperatures t_I and t_{II} for aqueous solutions of THF (X=0.02, 0.03, 0.05)

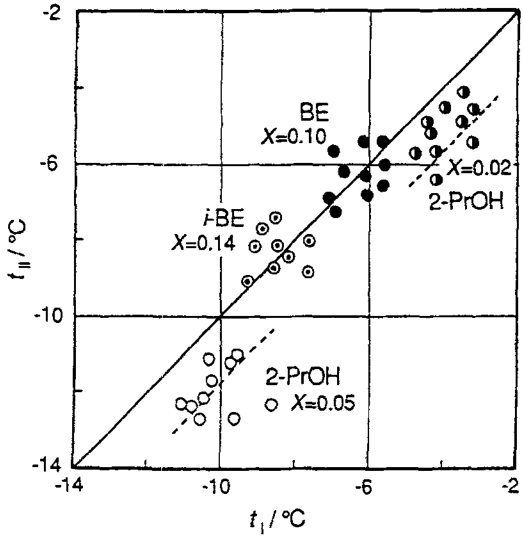

Fig. 5 Relationship between the supercooling temperatures t_I and t_{II} for aqueous solutions of 2-PrOH (X=0.02, 0.05), BE (X=0.10), and i-BE (X=0.14)

works around alkyl groups in solution II are partially destroyed by raising temperature. It is interesting to note that points A and B in Fig. 3 have the same thermodynamic variables. 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 thermally destroyed hydrogen-bonded water networks in the solution II of THF and 2-PrOH cannot easily revert to a state in the solution I within the time interval examined. The same phenomena were also observed for both $(n\text{-}C_4H_9)_4NCl$ and $(i\text{-}C_5H_{11})_4NCl$ solutions [3, 4]. However, for both BE and *i*-BE solutions the t_I values were almost equal to the t_{II} values. This behavior indicates that the state of water molecules is not affected by a liquid-liquid phase separation process.

Table 1 Entahalpies of mixing in kJ mol^{-1} of aqueous solutions of THF, 2-PrOH, BE, and *i*-BE (X=0.05) with acetone at 15°C

	Aqueous solutions			
	THF	2-PrOH	BE	*i*-BE
ΔH_I	66.0±0.5	76.4±1.0	72.4±0.8	75.4±0.9
ΔH_{II}	62.7±0.5	72.4±1.1	70.9±0.6	74.6±0.6
ΔH_I–ΔH_{II}	3.3±0.7	4.0±1.5	1.5±1.0	0.8±1.1

Enthalpies of mixing

The enthalpy changes when 0.2 g of an aqueous solutions of THF, 2-PrOH, BE, and *i*-BE with X=0.05 are mixed with 25 ml of acetone at 15°C are shown in Table 1. Similar data when the solvent is THF are shown in Table 2. 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 each solute. Tables 1 and 2 also include the differences between ΔH_I and ΔH_{II} , ΔH_I–ΔH_{II}. Tables 1 and 2 show that (1) for both aqueous solutions of THF and 2-PrOH, the differences ΔH_I–ΔH_{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; and (2) for both aqueous solutions of BE and *i*-BE, the differences $\Delta H_I - \Delta H_{II}$ are further small and cannot be discussed quantitatively because they are attached by similar amount of probable errors. These results for the BE and *i*-BE solutions coincide with the measurements of supercooling temperatures shown in Fig. 5.

It is interesting to note that, for aqueous solutions of THF and 2-PrOH, the ΔH_I–ΔH_{II} values are nearly equal to 3.4 kJ mol^{-1}. This value seems to represent the

Table 2 Entahalpies of mixing in kJ mol^{-1} of aqueous solutions of THF, 2-PrOH,and BE (X=0.05) with THF at 15°C

	Aqueous solutions		
	THF	2-PrOH	BE
ΔH_I	75.2±0.6	81.5±0.8	84.2±0.9
ΔH_{II}	72.3±0.4	78.1±0.5	83.0±0.5
ΔH_I–ΔH_{II}	2.9±0.7	3.4±0.9	1.2±1.0

energy difference of hydrogen-bonded water networks around one mole of either THF or 2-PrOH molecule between solutions I and II for the following reasons. In the final states of mixing of these aqueous solutions both water and solute molecules may be dispersed monomolecularly, because: (1) the molar ratios of solute:water: solvent are equal to 1:49:about 1000, and (2) solute–solvent interaction is expected to be relatively weak. Since the mole fraction of THF and 2-PrOH solution is 0.05, the value of 3.4 kJ per mole of solute corresponds to about 0.07 kJ per mole of water, which corresponds to 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 experiment. The value of 0.07 kJ per mole of water is fairly smaller than that when aqueous solution of $(n\text{-}C_4H_9)_4NCl$ is destroyed by raising temperature to 80°C (0.204 kJ per mole of water) [3] and is almost the same as that when aqueous solution of $(n\text{-}C_4H_9)_4NCl$ is destroyed by irradiation with ultrasonic waves (38 kHz, 20 min) (0.06 kJ per mole of water) [4].

Table 3 Entahalpies of mixing in kJ mol^{-1} of aqueous solutions of THF and 2-PrOH (X=0.05) with water at 15°C

	Aqueous solutions	
	THF	2-PrOH
ΔH_I	–4.85±0.02	–2.57±0.04
ΔH_{II}	–5.14±0.02	–2.80±0.01
ΔH_I–ΔH_{II}	0.29±0.03	0.23±0.04

The mixing processes of solutions I and II with water are essentially different from those with other solvents; the hydrogen-bonded water networks around nonpolar groups 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 mixing process with water are the same for both solutions I and II, the ΔH_I–ΔH_{II} value should be independent of the kinds of solvent, because both ΔH_I and ΔH_{II} simply indicate the difference of enthalpy between an initial state and a final state. The enthalpies of mixing of aqueous solutions of THF and 2-PrOH (X=0.05) with water at 15°C are shown in Table 3 in a similar manner as in Tables 1 and 2. Table 3 clearly indicates that the difference ΔH_I–ΔH_{II} is fairly small compared with those listed in Tables 1 and 2. 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 state, just as shown for states A and B in Fig. 3. Similar situations were also found for $(n\text{-}C_4H_9)_4NCl$ solutions in previous experiments [3, 4].

Conclusion

In order to observe more directly the structural organization of water molecule around an organic molecule in an aqueous solution, supercooling temperatures and enthalpies of mixing have been examined using two kinds of solutions (solutions I and II) of THF, 2-PrOH, BE, and *i*-BE. Solution I was made by keeping its temperature at 15°C and solution II by raising temperature to 80°C. The supercooling temperatures of solution I were found to be 2–3 degrees higher than those of solution II and enthalpies of mixing of solution I were slightly endothermic than those of solution II for aqueous solutions of THF and 2-PrOH. Significant differences between solution I and solution II could not be observed for aqueous solutions of BE and *i-BE.*

References

1 W.-Y. Wen, in R. A. Horn (Ed.), Water and Aqueous Solutions, Wiley Interscience, New York 1972, Chap. 15, p. 613.
2 I. M. Kloz, in M. Kasha and B. Pullman (Eds), Horizons in Biochemistry, Academic Press, New York 1962, p. 523.
3 H. Nakayama and C. Hayashi, Thermochim. Acta, 253 (1995) 77.
4 H. Nakayama, C. Hayashi and M. Endou, Bull. Chem. Soc. Jpn., 69 (1996) 1187.
5 H. Nakayama, Bull. Chem. Soc. Jpn., 54 (1981) 3717.
6 R. K. McMullan, M. Bonamico and G. A. Jeffrey, J. Chem. Phys., 39 (1963) 3295.
7 M. von Stackelberg and B. Meuthen, Z. Elektrochem., 62 (1958) 130.
8 H. Matsui and H. Nakayama, Bull. Chem. Soc. Jpn., 57 (1984) 2663.