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Detection of water–polar solvent interaction using melting of a eutectic

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Abstract

We focused on the eutectics of water and a lower alcohol or polar solvent, and investigated the relationship between the change in the solution structure and the melting peak of the eutectic in aqueous solutions of ethanol, propanol or DMSO. We found that the melting temperature and melting enthalpy of 0.05 alcohol molar fraction solutions were almost constant regardless of ultrasonic treatment, while the melting enthalpy of 0.10 alcohol molar fraction solutions fell to 81% (ethanol) and 46% (1-propanol) of the pretreatment value. The melting enthalpy of the eutectic of a polar solvent and water may be reduced by ultrasonic treatment in the liquid state. These results agree with the data from ^{17}O NMR of water and the absorption peak at 1150 nm for free water. These results show that water–polar solvent interaction can be detected by examining the melting of a eutectic of a polar solvent and water using sensitive DSC.
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Keywords: Eutectic of water and polar solvent; Differential scanning calorimetry (DSC); Water and polar solvent interaction; Alcohol; Solution structure

1. Introduction

Water and lower alcohols show characteristic properties due to the formation of hydrogen bonding networks in solution. For example, methanol, ethanol and propanol are completely miscible with water, and it is impossible to remove the last traces of water from these alcohols. The addition of alcohol to water decreases both the freezing and boiling points, and increases the vapor pressure and surface tension [1]. Recently, the structure of water–alcohol solutions over the whole composition region has been extensively studied by X-ray diffraction [2], NMR [3], mass spectrometry [4,5], dielectric measurements [6,7] and thermodynamics calculations [8,9]. These studies have focused on the change in the cluster structure formed by water and alcohol molecules as the composition of the solution varies. We reported observations which suggested such structural changes obtained using a high-frequency dielectric technique [10,11]. We found that water–alcohol interaction was affected by ultrasonic treatment of a water-rich solution, by studying near-infra-red (NIR) and ^{1}H NMR spectra. It is known that a lower alcohol such as ethanol forms a eutectic with water at lower temperature [1]. Dimethyl sulfoxide (DMSO) and *N*,*N*′-dimethylformamide (DMF), which are typical polar solvents, also form eutectics with water. We reported that the melting temperature and enthalpy of a eutectic of NaCl and water was influenced by the solution structure in dilute NaCl solutions [12]. In this study, we focused on the eutectics of water and lower alcohols or a polar solvent, and investigated the relationship between the change in the

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solution structure and the melting peak of the eutectic in aqueous solutions of ethanol, propanol or DMSO.

2. Experimental

Dehydrated ethanol, dehydrated 1-propanol and dehydrated DMSO were purchased from Wako Pure Chemical Industries, and used without further purification. The purity of these reagents was at least 99.5%. Water was purified with a Millipore Milli-Q SP system.

Measurements were made with an SII DSC Exstar6000 DSC100, a JEOL NMR JNM EX400, and aJASCO NIR V570. Ultrasonic treatment was performed using an automatic ultrasonic washer at 40, 80 and 120 W.

DSC measurements were made on aqueous polar solvent solutions. The solution was sealed in a silver metal container of 6 mm × 4 mm and weighed. The sample was first cooled to 130 K at 4 K/min and then heated at 4 K/min. A sapphire was used as a reference.

NIR measurements were made at room temperature at a range 900–1300 nm. Pure water was used as a reference. ^{17}O NMR measurements were made at 303 K operating at 54.10 MHz for ^{17}O. Spectra were recorded with probe spinning. ^{17}O spectra were recorded at a natural abundance of the ^{17}O isotope. D_2O was used as an external reference.

3. Results and discussion

Fig. 1 shows the melting curves for aqueous solutions of ethanol (a) and 1-propanol (b) with less than a 0.2 molar fraction of alcohol. With less than 0.08 of ethanol, and more than 0.08 of 1-propanol two endothermic peaks are observed, one at around 217 K (1-propanol) or 170 K (ethanol) and the other at around 273 K. The former small peak is attributed to melting of the eutectic of alcohol and water and the latter main peak is due to the melting of ice. With less than a 0.06 molar fraction of 1-propanol, the main peak is shifted to a higher temperature and a shoulder peak appears. With more than a 0.08 molar fraction of ethanol, a shoulder peak appears slightly above the melting temperature of the eutectic. Fig. 2 shows the NIR spectra of aqueous solutions of ethanol (a) and 1-propanol (b) with less than a 0.2 molar fraction of alcohol. Both spectra show isosbestic points of a peak assigned to $\nu_1 + \nu_2 + \nu_3$ for hydrogen-bonded OH of alcohol with water at around 1180 nm. These results suggest that the concentration region lower than 0.2 molar fraction of alcohol can be divided into two regions of greater or less than about 0.08 molar fraction. The former region is shown as region I, and the latter is region II. Considering the number of water molecules in contact with alcohol (n_h is 15 for ethanol and 17 for 1-propanol [13]), in region II there are no free water molecules in the solution. This is consistent with the X-ray diffraction data of an ethanol–water mixture. For all compositions, the degree of order (as indicated by the intensity of the diffraction peak) is higher than would be expected, with a pronounced structuring occurring just below 0.1 molar fraction [14].

Therefore, we investigated the effect of ultrasonic treatment on aqueous solutions of ethanol and 1-propanol with alcohol concentrations of 0.05 and 0.10 molar fractions. Table 1 shows the effect of ultrasonic treatment on the melting peak of a eutectic of ethanol or 1-propanol and water. The melting temperature and melting enthalpy of 0.05 alcohol molar fraction solutions were almost constant regardless of ultrasonic treatment, while the melting enthalpy of 0.10 alcohol molar fraction solutions fell to 81% (ethanol) and 46% (1-propanol) of the respective pretreatment values. These results suggest that the melting enthalpy of a eutectic of a polar solvent and water is reduced by ultrasonic treatment in the liquid state. If the solutions were stored for a long time, the melting enthalpy of the eutectic increased.

Table 1
Effect of ultrasonic treatment on the melting peak of a eutectic of a solution of ethanol or 1-propanol and water (molar fraction of alcohol, 0.05 and 0.1) (80 W, 10 min)

Alcohol (molar fraction)	Before treatment/after treatment	
	Melting enthalpy (J/g)	Melting temperature (K)
Ethanol (0.05)	11.9/11.9	203.5/203.4
Ethanol (0.10)	21.6/17.5	203.4/202.6
1-Propanol (0.05)	4.4/3.7	217.2/217.2
1-Propanol (0.10)	10.6/4.9	216.6/216.5

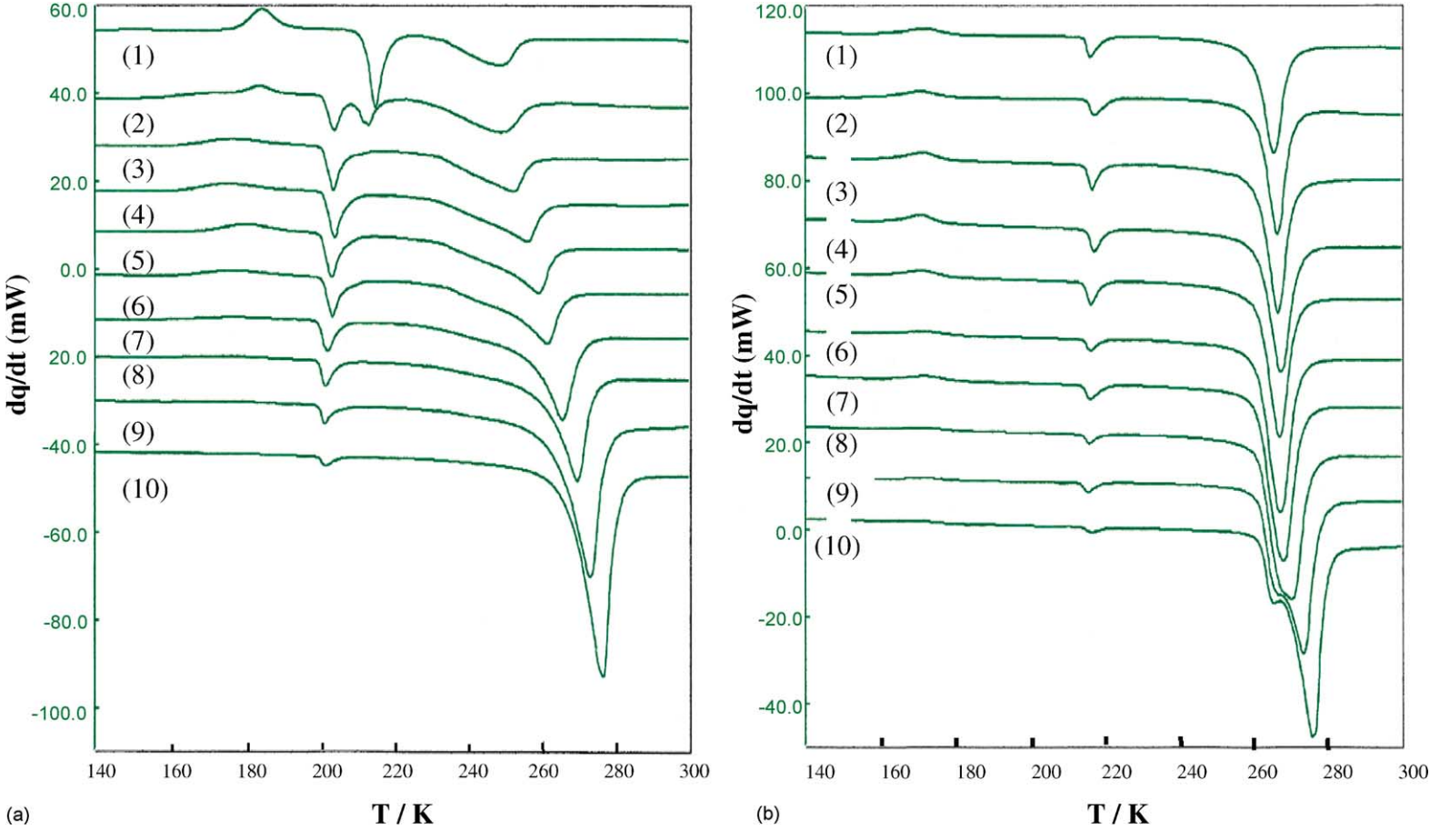

Fig. 1. DSC melting curves for aqueous solutions of ethanol (a) and 1-propanol (b) molar fraction of alcohol: (1) 0.20, (2) 0.18, (3) 0.16, (4) 0.14, (5) 0.12, (6) 0.10, (7) 0.08, (8) 0.06, (9) 0.04 and (10) 0.02.

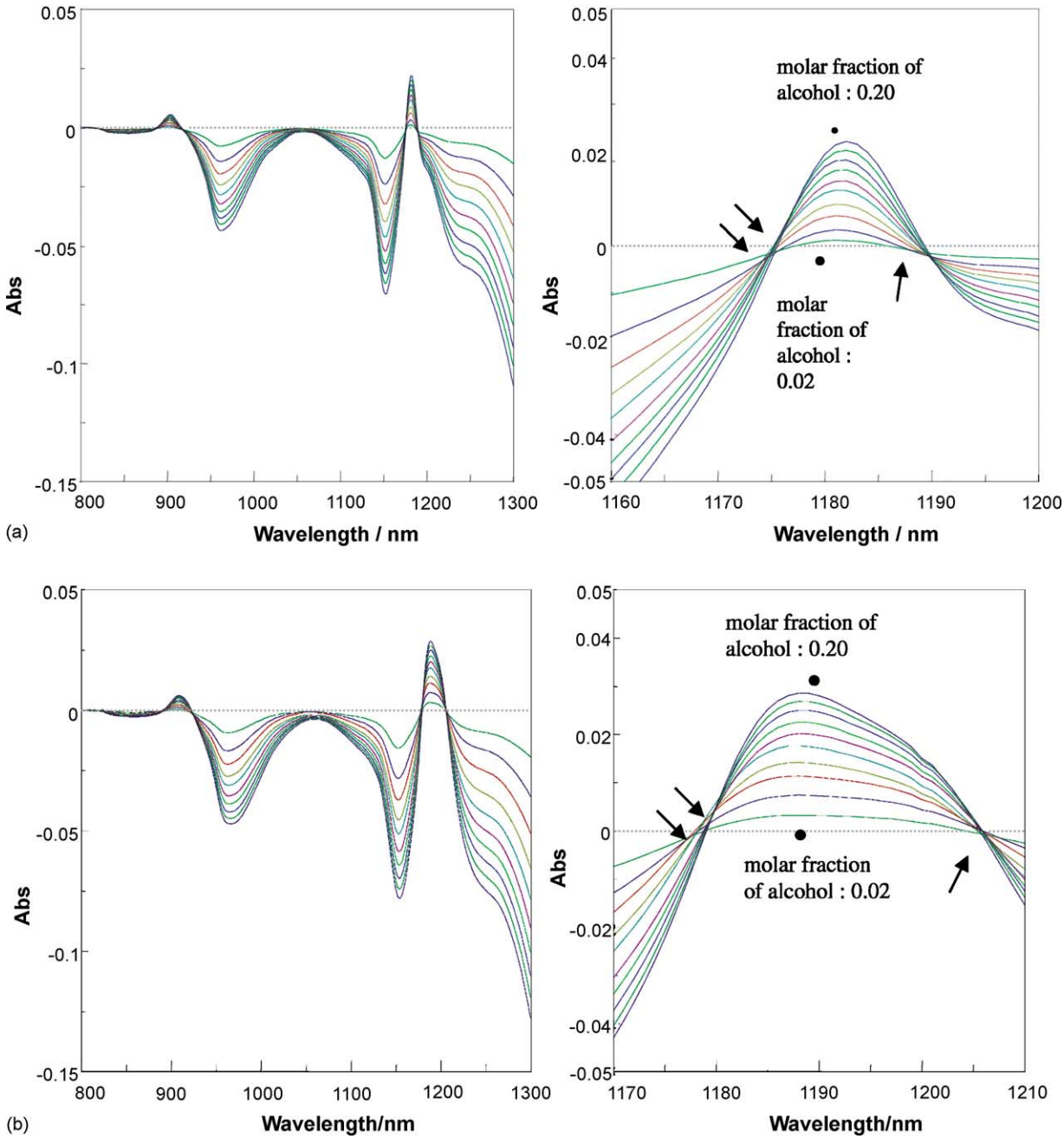

Fig. 2. NIR spectra of aqueous solutions of ethanol (a) and 1-propanol (b) molar fraction of alcohol: 0.02 to 0.20.

Next, we investigated the ^{17}O NMR and NIR spectra of this system to obtain information on the individual mixture components. Table 2 shows the data. The ^{17}O resonance peak of water in solutions with a 0.1 alcohol molar fraction was sharpened by ultrasonic treatment, while the sharpness of the peak with a 0.05 alcohol molar fraction was unaffected. In the case of the solution less than 0.2 alcohol molar fraction,

Table 2
Effect of ultrasonic treatment on the ^{17}O NMR and NIR data of a solution of ethanol or 1-propanol and water (molar fraction of alcohol, 0.05 and 0.1) (80 W, 10 min)

Alcohol (molar fraction)	Before treatment/after treatment			
	^{17}O NMR peak		NIR peak intensity (Abs)*	
	Half width (Hz)	T_2 (s)	960 nm	1150 nm
Ethanol (0.05)	113/108	$2.8 \times 10^{-3}/2.9 \times 10^{-3}$	−0.016/−0.016	−0.026/−0.024
Ethanol (0.10)	147/109	$2.2 \times 10^{-3}/2.9 \times 10^{-3}$	−0.028/−0.027	−0.044/−0.041
1-Propanol (0.05)	115/110	$2.8 \times 10^{-3}/2.9 \times 10^{-3}$	−0.019/−0.018	−0.031/−0.028
1-Propanol (0.10)	147/140	$2.2 \times 10^{-3}/2.3 \times 10^{-3}$	−0.031/−0.029	−0.050/−0.044

the resonance peak of alcohol does not clear because of alcohol–water interaction. So we focused on the resonance peak of water. The sharpness of the resonance peak is related to the spin–spin relaxation time, T_2. In Table 2, T_2 value of ^{17}O was also shown. The results show that water became more mobile with ultrasonic treatment in the case of a 0.10 molar fraction solution because the T_2 value of solution lengthened by ultrasonic treatment in the case of a 0.1 molar fraction solution compared to a 0.05 molar fraction solution. The absorption peak at 960 nm was assigned to $2\nu_1 + \nu_3$ for monomer water, and that at 1150 nm was assigned to $\nu_1+\nu_2+\nu_3$ for free water. The results show that the proportion of free water or water monomer increased upon ultrasonic treatment in the case of 0.10 molar fraction solutions. If the solution was kept for a long time, the solution structure gradually stabilized, as in the aging of an ethanol–water mixture. The water–alcohol interaction may have been weakened by ultrasonic treatment and the extent of the weakening in 1-propanol solution may have been greater than that in ethanol solution at a 0.10 molar fraction. The alcohol molecules in solution were completely hydrated by water molecules in region II. Therefore, the solution structure was not changed by ultrasonic treatment in the case of a 0.05 alcohol molar fraction solution. On the other hand, in the case of 0.10 molar fraction solutions, some alcohol molecules were not completely hydrated (region I). Therefore, the solution structure was changed by ultrasonic treatment and the proportion of free water increased. Our results showed that the melting enthalpy of the eutectic of water and alcohol correlated to the solution structure in the water-rich region.

We investigated the effect of the strength and duration of ultrasonic treatment on 0.10 molar fraction solutions. Table 3 shows the effects of treatment period and strength on the melting peaks of eutectics of ethanol or 1-propanol and water. Under these conditions, treatment at 80 W had the greatest effect.

In addition to ethanol and 1-propanol, polar organic solvents that are completely miscible with water were also investigated by DSC. The results showed that 2-propanol, *N*,*N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) form eutectics with water. Among these, only that with DMSO was affected by ultrasonic treatment. Tables 4 and 5 shows the results. The results were almost the same as those with alcohol. These results indicate that water–polar solvent interaction could be detected by melting of a eutectic of a polar solvent and water using sensitive DSC.

Table 3
Effect of the duration and strength of ultrasonic treatment on the melting peak of a eutectic of water and a polar solvent (molar fraction of polar solvent −0.1) (melting enthalpy (J/g)/temperature (K))

10 min	1-Propanol	Ethanol	80 W	1-Propanol	Ethanol
40 W	7.7/216.5	20.9/202.8	0 min	11.0/216.8	21.6/204.6
80 W	4.9/216.8	18.0/202.6	1 min	4.8/216.9	17.8/204.2
120 W	5.1/216.4	20.2/203.0	10 min	4.9/216.9	18.2/202.8

Table 4
Effect of ultrasonic treatment on the melting peak of a eutectic of a solution of DMSO and water (molar fraction of DMSO, 0.05 and 0.1) (80 W, 10 min)

DMSO (molar fraction)	Before treatment/after treatment	
	Melting enthalpy (J/g)	Melting temperature (K)
0.05	13.7/11.6	212.5/212.2
0.10	42.2/33.0	213.6/213.4

Table 5
Effect of ultrasonic treatment on the ^{17}O NMR data of a solution of DMSO and water (molar fraction of DMSO, 0.05 and 0.1) (80 W, 10 min)

DMSO (molar fraction)	Before treatment/after treatment	
	Half width (Hz)	T_2 (s)
0.05	95/95	$3.4 \times 10^{-3}/3.4 \times 10^{-3}$
0.10	113/107	$2.8 \times 10^{-3}/3.0 \times 10^{-3}$

References

[1] V. Gutmann, G. Resch, Lecture Notes in Solution Chemistry, World Scientific, Singapore, 1995, pp. 117–120.
[2] K. Nishikawa, T. Iijima, J. Phys. Chem. 94 (1990) 6227.
[3] R. Ludwig, Chem. Phys. 195 (1995) 329.
[4] N. Nishi, S. Takahashi, M. Matsumoto, A. Tanaka, K. Muraya, T. Takamuku, T. Yamaguchi, J. Phys. Chem. 99 (1995) 462.
[5] M. Matsumoto, N. Nishi, T. Furusawa, M. Saita, T. Takamuku, M. Yamaguchi, T. Yamaguchi, Bull. Chem. Soc. Jpn. 68 (1995) 1775.
[6] S. Mashimo, T. Umehara, J. Chem. Phys. 95 (1991) 6257.
[7] M. Tabellout, P. Lanceleur, J.R. Emery, D. Hayward, R.A. Pethrich, J. Chem. Soc., Faraday Trans. 86 (1991) 1493.
[8] Y. Koga, W.W. Siu, Y.T.H. Wong, J. Phys. Chem. 94 (1990) 7700.
[9] A. Laaksonen, M. Kulmala, J. Chem. Phys. 95 (1991) 6745.
[10] T. Takei, Y. Sugitani, C. Amano, Y. Nishimoto, Bunseki Kagaku 45 (1996) 903.
[11] T. Takei, C. Amano, Y. Nishimoto, Y. Sugitani, Anal. Sci. 13 (1997) 1043.
[12] Y. Nishimoto, J. Therm. Anal. 40 (1993) 413.
[13] H. Uedaira, Mizu no Bunshikougaku (Molecular Industry of Water), 1998, p. 149 (in Japanese).
[14] F. Franks (Ed.), Water, vol. 2, Plenum Press, New York, 1973, p. 22.