Frozen bound water melting induced cooperative hydration of poly(vinyl methyl ether) in aqueous solution

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Summary

Poly(vinyl methyl ether) aqueous solution (30 wt.-%) at low temperature has been investigated by DSC and FTIR spectroscopy. Below −20°C, there are two types of ice formed by free water and frozen bound water respectively. When the ice formed by frozen bound water melts, the PVME begins to form hydrogen with water. A cooperative hydration phenomenon is observed in this system between −20 ~ −6°C during heating. FTIR data also show that hydrogen bonds between water molecules and polymer groups are broken completely before the cooperative hydration happens. This indicates that the unfrozen bound might not exist in 30 wt.-% PVME aqueous solution at low temperature.

Introduction

Poly(vinyl methyl ether)(PVME) aqueous solution is known to have lower critical solution temperatures(LCST) at moderate temperature around 35°C and, above the temperature, the solution separates into two phases [1-3]. This phenomenon has been extensively investigated by using DSC [4,5], NMR [6] and FTIR [7] et al, techniques. It has been confirmed that the PVME molecule in aqueous solution forms a complex with water. Maeda et al [8] have given evidence for the formation of a stable molecular complex with 2.7 molecules of water per repeating unit of the PVME. With a higher overall water content, a higher degree of hydration is suggested with up to five water molecules per repeat unit of the PVME. Nies et al. [5] have also proposed that a molecular complex with maximum of two water molecules per repeating unit is formed by investigating the concentration dependence of the melting point of water and the glass transition in the PVME aqueous solution. A temperature-induced cooperative destruction of the complex around LCST has been found by using near-infrared, viscometric and calorimetric measurement [8].
It is important to note that the study of this complex at low temperature can promote our understanding about the different states of water in polymer aqueous solution. Thus, this has provoked keen interest in many researchers over the past decades [9-11]. However, the stability of the PVME/water complex at low temperature is still unclear. The study of this system at low temperature has been relatively few till now.

Usually, calorimetric methods such as differential scanning calorimetry (DSC) monitor the gross phase changes of water in polymers. Such thermodynamic measurements permit the characterization of hydrated systems without recourse to detailed molecular models. FTIR spectra, on the other hand, can provide site-specific molecular information between water and polymer. In the work, IR spectroscopy and DSC are thus used to investigate the PVME aqueous solution (30 wt.-%). According to the changes in the hydrogen bond between the ether oxygen of the PVME and water and the hydration states of methyl group, the stability of the PVME/H_2O complex at low temperature is studied and a cooperative hydration phenomenon is observed between $-20 \sim -6°C$ during heating.

Experimental

Material

Poly(vinyl methyl ether) (PVME), as pure nonaqueous solid, was obtained from Aldrich. The sample was kindly supplied by Prof. Nies. The molecular weight of the polymer, determined by gel permeation chromatography, was $M_W = 20Kg/mol$. The PVME solution was prepared by incubating the polymer in deionized water for several days at room temperature to equilibrium. Concentrations are given in polymer weight fraction.

FTIR Measurements

All spectra were recorded on a Bruker EQUINOX 55 spectrometer and processed by the Bruker OPUS program. A sample solution was put between two CaF_2 windows without spacers and the sample thinness was adjusted to make the maximum absorbance of target IR bands to smaller than 2 absorbance units. The background spectrum for one cycle of the measurement was obtained with a clear CaF_2 window. A Bruker P/N 21525 series variable temperature cell was used.

### Differential Scanning Calorimetry (DSC) Measurement

A Perkin-Elmer 7 differential scanning calorimeter was used to detect the phase transition of water absorbed in the polymer samples. DSC curves were obtained by cooling the sample from room temperature to -50°C and subsequently reheating to room temperature at the scanning rate of 10°C min⁻¹.

Results and discussion

1.   Behavior of water in PVME solution at low temperature

In this work, a 30 wt.-% PVME aqueous solution is chosen. In the sample, the number of water molecules on each repeating unit of PVME is about 7.5 which is greater than the maximum number of water molecules in the polymer-water complex per repeat unit of PVME proposed by Maeda [8] (5 H_2O) and Nies [5] (2 H_2O). Therefore, there is free water in addition to the polymer-water complex. A typical thermogram of this sample is represented in Figure 1. Two endotherms of water melting are observed in the DSC thermograms, one at ca. 0°C (the melting point of normal ice), and the other at a lower melting temperature around -15°C. This indicates that there are at least two states of frozen water in the solution. The phenomenon has also been found in many

other systems, especially in hydrogel [12,13].
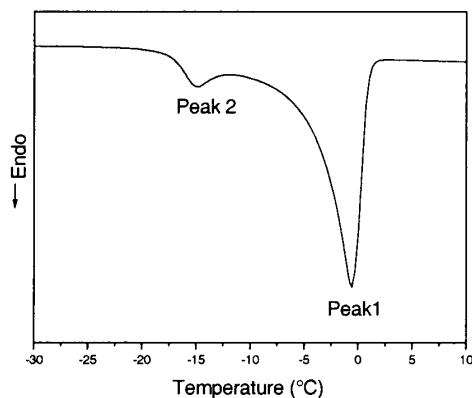
Figure 1. DSC curve of the system PVME/water; PVME content: 30 wt.-%
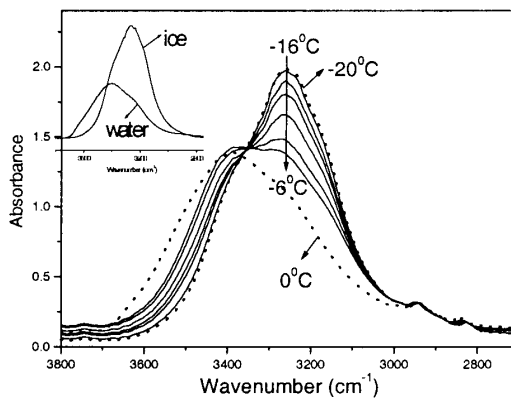
Figure 2. IR spectra of H_2O in 30 wt.- % PVME solution measured at −16,-14,-12, -10, -8, -6°C, dot line shows the IR spectrum measured at −20 and 0°C respectively. Inset: IR spectra of ice and pure water

Higuchi et al. [14] have proposed that water is present in three states in hydrophilic polymer matrices: (1) unfrozen bound water, (2) frozen bound water and (3) free water.The unfrozen bound water adsorbed in polymer will not crystallize even when the swollen sample is cooled down to -100°C. The frozen bound water and the free water will form crystals at a temperature lower than 0°C and at 0°C respectively. Obviously, in the case of PVME aqueous solution, Peak 1 corresponds to the crystal of free water and the part of water molecules melting around -15°C, in Peak 2, is assigned to the frozen bound water. The melting temperature of the frozen bound water is often observed between -30 ~ 0°C and the depression is commonly ascribed to a weak interaction of the water with the network polymer chain [15] and/or capillary condensation [16]. Traditionally, the content of unfrozen bound water is estimate on the basis of the assumption that the fusion enthalpy of frozen bound water is taken to be the same as that of free water (334J/g) [17]. However, the assumption is inappropriate. The heat of fusion in polymer solution should be substantially lower than that of pure bulk ice. Frommer et al.[18] have suggested that a lowering of the heat of fusion is resulted from the difference in heat capacity between the pure bulk water and the water in the membranes. Moreover, the hydration of PVME is an exothermal process, which also results in the lack of melting enthalpy. Therefore, only by the fact that the fusion enthalpy of frozen bound water in this system (about 154 J/g) is far lower than the pure bulk water (334 J/g), it is hard to conclude that unfrozen bound water exists in the sample. Further discussion will be given below.

Figure 2 shows the changes in the profiles of IR spectra of water during the melting of frozen bound water. The Inset spectra display the IR absorption of pure water at a lower frequency and that of pure ice at a higher frequency. Below -16°C, the IR spectra of water are almost unchanged with the changed temperatures and they are similar to that of pure ice. It means that unfrozen bound water may not exist in this sample. At the range of -16°C ~ -6°C, the IR spectra change obviously. The intensities of the 3250 cm^{-1} band decrease largely and that of the 3400 cm^{-1} enhance with the increase of temperature. That is, an increase in temperature results in a decrease of absorption at lower frequency but an increase of absorption at higher frequency. It

illustrates the frozen bound water would melt from -16 to -6 °C. Upon further raising the temperature, the ice formed by free water melts quickly and the spectra profiles become similar to that of pure water.

## 2. *Change in C-H Stretching bands and C-O Stretching Bands of PVME during the melting of the frozen bound water*

Furthermore, the molecular behavior of the PVME and the interaction of the polymer with water are checked at the temperature range of $-20 \sim 0°C$, at which the DSC peaks occur. The sample is cooled to -50°C and then heated back to room temperature at the rate of 1°C/min. In the process of heating, the IR spectra are recorded in Figure 3.
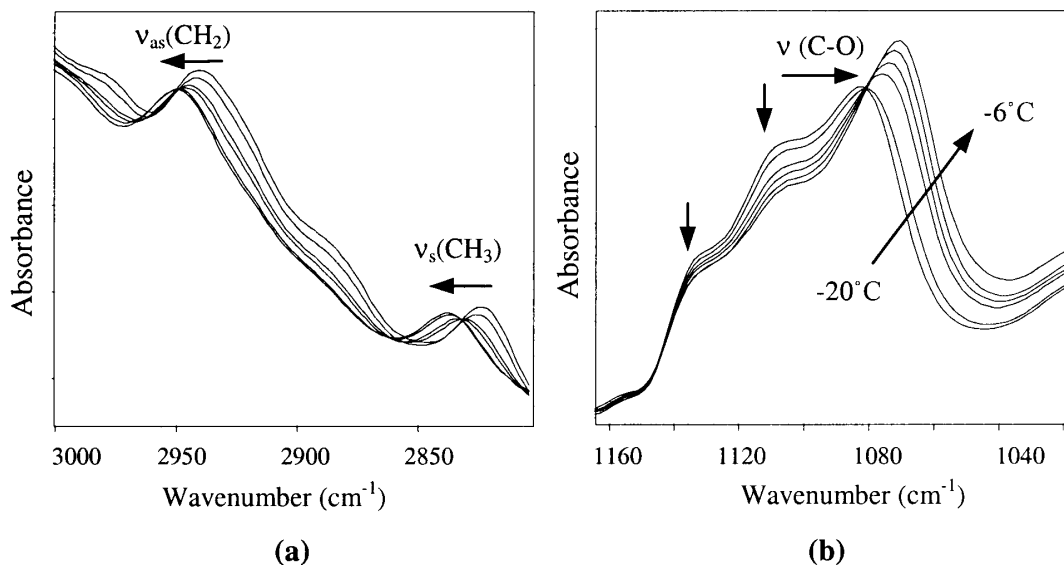
**Figure 3.** IR spectra of PVME in water in the 3000-2800 cm^{-1} (a), and in the 1200-1000 cm^{-1} (b) at -20, -16, 14, -12, -10, -6°C, the arrows show the direction of heating

It is interesting to find that C-H stretching bands and C-O stretching bands of PVME starts to change at -20°C, which is lower than that of O-H stretching bands of water (at -16°C). We notice that the glass transition of the PVME is at about -19°C. It imply that the enhancement of the mobility of the PVME molecules promotes the interaction between the polymer and the frozen bound water, and thus inducing the melting of the ice formed by the frozen bound water. Figure 3a shows the change in C-H stretching bands of the PVME in aqueous solution during the melting of the frozen bound water. Maeda et al [7] have examined the phase transitions of PVME aqueous solutions at 35°C in D$_2$O and propose that large red shifts of the $\nu_s(CH_3)$ and $\nu_{as}(CH_2)$ bands of the PVME above the LCST are due to the dehydration of the methyl group and the break of hydrogen bond between alkyl group of the polymer and water. So a blue shift of C-H stretching bands can be explained by the hydration of an alkyl group. IR spectra of the sample in the 1200-1000 cm^{-1} region, in Figure 3b, are measured in the temperature range from $-20 \sim -6°C$. The 1106 and 1136 cm^{-1} bands with a change in their intensities but not their positions are insensitive to environment, whereas the 1083 cm^{-1} band has been shown to be sensitive to the interaction of the ether oxygen and conformation around the C-O bond [19]. Maeda [7] also points that the 1083 cm^{-1} band essentially involves pure C-O stretching and found that the blue shift of the band

induced by the phase separation indicates the break of hydrogen bond between the ether oxygen and water. In other words, the red shift means the form of hydrogen bond between ether oxygen of the polymer and water.
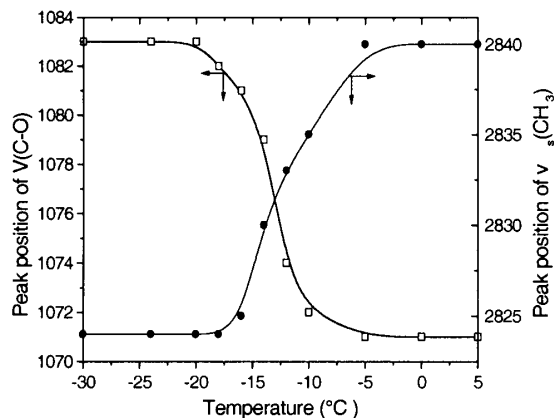
Figure 4. A plot of the wavenumber of the v (C-O) and $v_s(CH_3)$ as a function of temperature
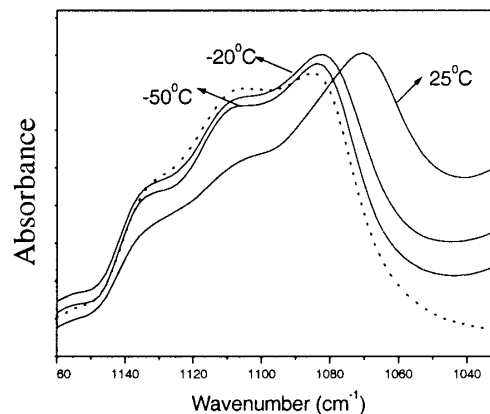
Figure 5. The C-O-C stretching region of the IR spectra of 30wt.-% PVME aqueous solution at various temperature. Dot line shows the IR spectra of pure PVME

The peak positions of the $v_s(CH_3)$ band and the v (C-O) band are plotted as a function of temperature in Figure 4. They both exhibit critical changes in the temperature range from $-20 \sim -6°C$ and the sigmoidal shift of the peak positions are observed. The sigmoidal curve is a characteristic of cooperative phenomena. Thus, it is inferred that there is a cooperative formation of a specific polymer-water complex. Rowland and Kuntz [9] recognized an emerging hierarchy of interactions for water in proteins (and, perhaps, for polymers in general), and listed as follows in order of decreasing strength: ion-ion > water-ion > water-polar = polar-polar = water-water > water-hydrophobic. Therefore, there is a possibility of a stepwise hydration. That is, the ether oxygen is first hydrated at a relatively low temperature and then the methyl group is hydrated at a higher temperature. However, it is interesting to find in Figure 4 that hydrations of the methyl and the ether groups proceed simultaneously.

It is also note that, below -20°C, there is no significant difference between the peak positions of the v (C-O) and $v_s(CH_3)$ bands of PVME in this system and those of the pure PVME solid. Figure 5 shows the C-O-C stretching region of the FTIR spectrum of 30wt.-% PVME aqueous solution at various temperatures. Although the spectra profile of the sample at $-20°C$ and $-50°C$ are not the same as that of the pure PVME sample, their peak positions are almost identically (at 1083 cm^{-1}). As mentioned above, the peak position of v (C-O) is sensitive to the hydration and dehydration of PVME. The small profiles change of this band should be attributed to conformation change induced by temperature et al [19]. The peak position of $v_s(CH_3)$ also shifts to that of pure PVME at low temperature (Figure not shown). These data show that PVME is dehydrated completely at temperature below -20°C. According to this, we propose that the unfrozen bound water should not exist in this system. The result is very different from that reported by Meeussen et al [5]. They believe that in the higher water concentration range, in which crystallization of water can take place, a certain fraction of water is still not able to crystallize. This dehydration of PVME at a

low temperature induced by crystallization of the frozen bound water is also different from that of PVME at temperature above the LCST. In that case, only partial dehydration of the ether group occurred although most of the methyl was dehydrated and there were strong interactions among PVME chains during this transition [7]. However, in the narrow and fixed polymer interstices below -20°C, the hydrogen bonds between water molecules and polymer groups are broken completely.

Conclusion

The study of the hydration of Poly(vinyl methyl ether) in aqueous solution at low temperature has been carried out by DSC and FTIR spectroscopy. The comparison of DSC and IR data provides an interesting insight into the role of water in hydrated PVME samples. Below -20°C, there are two types of ice: one is formed by free water and the other is formed by frozen bound water in the 30% PVME solution. IR data show that there are no hydrogen bonds between water molecules and polymer groups. Therefore, the polymer is dehydrated completely at temperature below -20°C. According to this, we speculate that unfrozen bound water maybe not exist in this system. This conclusion needs further confirmation by other techniques. When the ice formed by frozen bound water melts, the PVME begin to form hydrogen with water and a cooperative formation of a specific polymer-water complex is observed. Further discussion on the concentration dependence of the states of water in PVME aqueous solution will be published elsewhere.

References

1. F. Franks (1983) Chemistry and Technology of Water-Soluble Polymers. Plenum Press
2. Horne. R. A, Almeida. J. P, Day. A. F, Yu. N. T (1971) Journal of Colloid and Interface Science 35: 77
3. H. Schafer-Soenen, R, Moerkerke, H. Berghmans, R. Koningsveld (1997) Macromolecules 30: 410
4. Schild. H. G, Tirrell. D. A (1990) J. Phys. Chem 94:4352
5. Meeussen. F, Bauwens. Y, Moerkerke. Nies. R, Berghmans, H (2000) Polymer 41:3737
6. Karl-Fr. Arndt, Thomas Schmidt, Heike Menge (2001) Macromol. Symp 164:313
7. Maeda Y. (2001) Langmuir 17:1737
8. Maeda. H (1994) Journal of polymer science: Part B: Polymer Physics 32:91
9. S. P Rowland (1980) Water in Polymers. American Chemical Society: Washington DC
10. Nathaniel Pribble. R, Timothy S. Zwier (1994) Science 265:75
11. Florian Muller-Plathe (1998) Macromolecules 31:6721
12. Hodge, R. M, Edward, G. H, Simon, G. P (1996) Polymer 37, 1371
13. Cha, W. -I, Hyon, S. -H, Ikada, Y (1993) Makromol. Chem. 194: 2433
14. Higuchi. A, Komiyama. J, Lijima. T (1984) Polym Bull 11: 203
15. Taniguchi. Y, Horigome. S (1975) J. Appl. Polym. Sci 19: 2743
16. Burghoff. H. G, Pusch. W. J (1979) J. Appl. Polym. Sci 23:473
17. Nakamura. T, Hatakeyama. T, Hatakeyama. H (1983) Polymer 24: 871
18. Frommer. M. A, Lancet. D (1972) J. Appl. Polym. Sci 16:1295
19. Lu. F. J, Benedetti, E, Hsu. S. L (1983) Macromolecules 16:1525