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States of water in different hydrophilic polymers — DSC and FTIR studies

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Abstract

The structure of water molecules sorbed in different hydrophilic polymers was studied by DSC and FTIR. The obtained data shows that, first, the sorbed water molecules are directly bound to the hydrophilic site to form non-freezable water. Then, beyond a certain water content threshold, the sorbed water molecules become freezable, but with a melting point lower than 0°C, due to their location in the second hydration layer. Bulk-like water which can be frozen at 0°C appears at higher water contents, and the two types of freezable water finally merge together at very high water contents. The average number of non-freezable water molecules per site depends on the chemical nature of the polar site: ca. 1 for a hydroxyl, and 4.2 for an amide group. For a polymer with carboxylate sites, it increases with the size of the alkaline counter-ion of the site, due to the increasing ability of the carboxylate counter-ion pair to undergo dissociation. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Water; Hydrophilic polymer; Hydrogen bond

1. Introduction

Due to the modification of the structure of polymer materials after water sorption, the mechanical and the physical properties of hydrophilic polymers can vary significantly with the water activity in the surrounding medium. Upon water absorption, small or less perfect polymer crystallites can be destroyed [1]. The materials glass transition temperature (T_g) decreases sharply with the water content in the polymer materials [2].

Hydrophilic polymers are currently used to prepare membranes for the dehydration of alcohol and organic solvents by pervaporation. The absorbed water, which acts as a plasticizer in hydrophilic polymers, increases the mobility of the chains and decreases the glass transition temperature of the considered polymer. Thus, water absorption favors the permeability but modifies the selectivity to water in various solvents in the mixture permeation through these membrane materials [3,4].

Water absorbed in a hydrophilic polymer presents thermodynamic properties somewhat different from those of water in the bulk liquid phase [5–8]. For example, water absorbed in this type of polymer does not crystallize at 0°C. Higuchi et al. [9,10] showed that the heat (endotherm) for the melting of water crystals in PVA is 9% higher than that for water crystallization, when the content of water absorbed in PVA exceeds 60 wt%. Based on various thermodynamic properties of water absorbed in hydrophilic polymer, they proposed that water is present in three states in hydrophilic polymer matrices: (i) non-freezable bound water, (ii) freezable bound water, (iii) free water. The non-freezable bound water absorbed in polymer does not crystallize even when the swollen sample is cooled down to −100°C. The freezable bound water crystallizes at a temperature lower than 0°C, while the free water crystallizes at 0°C.

The 'anomalous' behavior of water in polymer materials can be attributed to the effect of capillary condensation, the confinement of water clusters by polymer chains, [11,12] or the strong interactions of the water molecules with the polar groups of the hydrophilic polymer, [13,14] either directly or via other water molecules. The latter are the cause for the origin of the term 'bound' in the name of the two first states of the absorbed water. Hirata et al. [15] called this type of water 'hydration water' but logically both the non-freezable bound water and the freezable bound water are hydration water; the term 'hydration water' is thus not suitable when both of them are present in the polymer.

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Generally speaking, the investigations on the states of water in a polymer must give valuable information on the sorption, diffusion and permeation properties of molecular species in hydrophilic polymers. Most of the works regarding water crystallization and ice melting have been carried out using differential scanning calorimetry (DSC) [11,12] and to a lesser extent, NMR [16,17]. Recent ^{17}O NMR data showed that there is only an average ^{17}O spin–lattice relaxation time for different types of water. This relaxation time decreases (i.e. the water mobility increases) with increasing 'hydration water' content, and the dissolved oxygen permeability through the swollen polymer is the lowest when the fraction of 'hydration-water' is the highest [15]. The DSC results suggested that there are close relationships between the water crystallization and the ice melting properties. However, each work dealt with a single chemical nature of the polymer (or copolymer), and it is not known how the quantity of water in each state varies with both the water content in the polymer material and the nature of the hydrophilic polymers.

In this paper, our attention is focused on the water absorbed in a polymer taken from two polymer groups. One group consists of poly(vinyl alcohol) of different hydrolysis degrees, the other consists of poly(ethylene)-*g*-acrylic acid membranes (PE-*g*-AA) with different counterions for the acid group. We expect that the polymers from these two groups have sufficiently different chemical structures, while those from the same group have a gradual change in the chemical properties, to allow us to obtain significant variations in the states of water and in their quantity. Infrared spectroscopy was performed to give complementary information on the water–polymer site interaction.

2. Experimental

2.1. Materials

Poly(vinyl alcohol) (PVA) samples of different hydrolysis degrees were supplied by Janssen Chimica. The polymers were atactic and their M_w (weight average molecular weight), as quoted by the manufacturer, is ca. 95 000, e.g. 2050 monomer units per chain on an average. Poly(vinyl pyrrolidone) of M_w 360 000 was supplied by Fluka.

Poly(ethylene)-*g*-acrylic acid membranes were kindly provided by Morgane Ltd. Its total ion-exchange capacity is ca. 3 equiv. kg^{-1} and the dry thickness of the membrane in Na$^+$ acrylate form was 35 μm.

2.2. Sample preparation

Homogeneous solutions of 10 wt% PVA were prepared by dissolving PVA powder in boiling water under moderate stirring for 2 h. The solutions were filtered to remove insoluble impurities then cast on polystyrene plate at room temperature. The quasi-dry PVA films were transferred to a vacuum oven at 60°C for 30 h to remove the residual solvent. The films obtained in this way had a thickness of ca. 1 mm. The dried samples were stored in a desiccator over 4 Å molecular sieve until their use.

To obtain the acid form of the PE-*g*-AA membrane, the sample was treated with a HCl solution, then thoroughly washed with distilled water. The alkaline acrylate membranes were prepared by titration of the membrane in the acid form with an appropriate alkaline aqueous solution, followed by the steps of washing and vacuum drying.

2.3. DSC measurements

Each dried sample (about 10 mg) was weighed in an aluminum pan designed for volatile samples. A determined amount of water was added to each sample by a microsyringe and then the pan was tightly sealed. Each sample pan was conditioned at 303 K for 24 h to obtain the sorption equilibrium state. The water content in each sample was calculated as follows:

$$C_w = W_w/(W_w + W_p) \quad (1)$$

here W_w is the mass of added water, and W_p that of the dry polymer.

The measurement was repeated several times with the same protocol to check the reproducibility. After the DSC measurement, the pan was weighed in order to ensure that there is no loss of weight (due to water vapor escaping from the pan).

A Mettler DSC 30 differential scanning calorimeter equipped with a cooling device was used to measure the phase transition of water sorbed in the polymer samples. DSC cures were obtained by fast sample cooling from room temperature to 173 K, followed by a reheating to room temperature at the scanning rate of 10 K min^{-1}. The mid-point of the heat capacity transition range was taken as the T_g.

The crystallization and melting temperatures of water sorbed in the sample were determined from the temperature at the maximum point of the corresponding enthalpy peaks. The mass of a type of freezable water was obtained as:

$$W_c = Q/\Delta H \text{ (g)} \quad (2)$$

where ΔH is the melting enthalpy of this type of water, assumed to be the same as that of bulk water ($\Delta H = 333.5\ J\ g^{-1}$) [18], and Q is the heat absorbed during the melting process. Q was calculated according to the area of the endothermic peak. This procedure for freezable water calculation does not take into account the difference in the melting enthalpies of ice of different crystal structures (I, Ic, II and III). However, even in the case where the difference in the melting enthalpies of ices is the largest (312 J g^{-1} for ice III instead of 314 J g^{-1} for ice I), the maximum error in the calculated amounts of freezable water is only 6.6%.

The mass of non-freezable bound water was obtained from the difference between the mass of absorbed water and that of the total mass of freezable water:

$$W_{nc} = W_t - W_c \quad (3)$$

2.4. IR measurements

The membrane samples equilibrated with an atmosphere at different humidity degrees were used for infrared (IR) measurement. FTIR spectra recorded on a Nicolet Magna-550 spectrophotometer. The ATR (attenuated total reflectance) method with a ZnSe prism was used. At least 256 scans were performed for each measurement. The resolution in wavelength was 2 cm^{-1}.

3. Results and discussion

3.1. Behavior of water in hydrophobic polymers

The quantities of water absorbed in hydrophobic polymers like poly(dimethylsiloxane) (PDMS) or poly(vinyl acetate) (PVAc) were very small (less than 0.1 wt% for PDMS, and less than 3 wt% for PVAc, at equilibrium in liquid water at 25°C), due to their high hydrophobicity.

DSC studies highlighted the absence of any solid–liquid phase transition in the water-saturated PDMS samples in the temperature range from −130 to 10°C. As there was negligible water–polymer affinity, such a behavior was probably due to the very low water concentration in PDMS. Water molecules were so far away from each other in the PDMS matrix that they could not get together to form ice crystals in the cooling step.

Due to the higher water sorption by PVAc at saturation in liquid water, a peak of ice melting at ca. 0°C was observed on the polymer DSC thermogram (Fig. 1). The quantity of freezable water was ca. half of the total water quantity absorbed in the polymer. The rest of absorbed water, which was non-freezable, corresponds to ca. one water molecule per acetate site on the average. The existence of non-freezable water in the polymer suggests that the interactions between a water molecule and a small fraction of the polar carboxyl groups in PVAc are strong enough to prevent water to move to other places to form ice crystals when the sample is cooled down to low temperatures. These interactions would be well-oriented hydrogen bonds between water (H-bond donor) and the carboxyl groups (H-bond acceptor), which were locally in a favorable configuration.

The presence of bulk-like water (with ice melting point of ca. 0°C) can be explained by the formation of water clusters in water-saturated PVAc. An alternative to this explanation is that water molecules were dispersed mono-molecularly in the polymer, but upon cooling, water molecules, which are close enough to each other, get together to form small ice crystals. This would be eventually possible due to low polymer–water interactions.

The other case in which there are only two states of water, i.e. non-freezable water and bulk-like water, is that of the perfluorinated ionomer membranes [15]. Like PVAc, these membranes have a large fraction of hydrophobic groups.

3.2. Influence of polymer chemical structure on the quantity of non-freezable bound water in hydrophilic polymers

Crystallization as well as melting of water in hydrophilic polymers are much more complex. At low water content, all the sorbed water molecules are non-freezable (no melting point detected). This leads first to a linear increase in the ratio of the number of sorbed water molecules to that of polymer unit with the water content in the hydrophilic polymer (Fig. 2).

In the study of PVA samples with different quantities of absorbed water, we observed that part of the water began to crystallize only when the water content is above a characteristic threshold (Fig. 2). This part of water has been named freezable-bound water [9], because of its low melting point compared with that of bulk water. When the quantity of

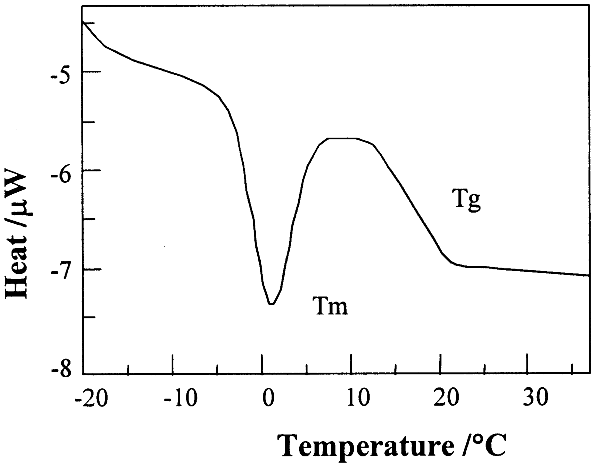


Fig. 1. DSC curve of the water absorbed in PVAc. Water content: 3%; heating rate:10 K min^{-1}.

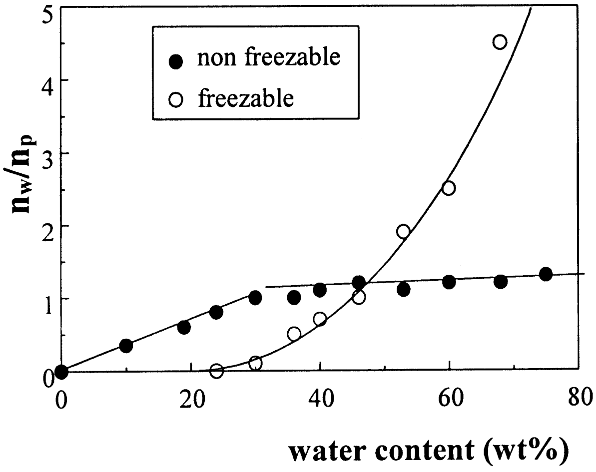
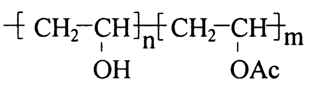
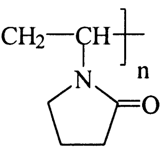
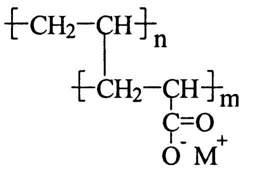


Fig. 2. Variation of the quantity of non-freezable bound water and that of the freezable-bound water as a function of water content in PVA.

Table 1
Molar ratios of non-freezable bound water in different polymers

Polymers	Unit structure	n_{wnc}/n_p
PVA100	 $-\left[CH_2-\underset{OH}{CH}\right]_n\left[CH_2-\underset{OAc}{CH}\right]_m$	0.8
PVA 95		1.1
PVA 88		1.2
PVP		4.2
PE-*g*-AA$^-$K$^+$		4.9
PE-*g*-AA$^-$Na$^+$		4.2
PE-*g*-AA$^-$Li$^+$		1.9

absorbed water increases, the content of freezable-bound water also begins to increase, but the quantity of non-freezable water remains constant. The results showed that the quantity of non-freezable water absorbed by PVA is practically constant even when the water content in polymer is very high (50 wt%). As far as the nature and the structure of polymer are concerned, the maximum quantity of non-freezable (i.e. the threshold for freezable-bound water formation) is a characteristic value. For PVA, this value is ca. 25 wt% water content. It should reflect on the ability of the polar groups to interact with water molecules in the polymer matrix. This ability would depend on the physico-chemical affinity of the polymer groups to water, the free space available in the vicinity of the sites as well as the local elastic resistance of the chains to a swelling deformation stress.

Table 1 shows that the calculated values of the maximum number of non-freezable water molecules per polar site vary greatly with the nature of the polymers. For instance, it is close to 1 in the case of PVA, suggesting a 1:1 interaction between a water molecule and a hydroxyl group. The smaller value for 100% hydrolysis degree PVA than for the 88% one can be explained by the larger fraction of OH groups involved in the intra-crystallite hydrogen bonds in PVA crystallites, which are present in larger proportion in PVA100. The molar ratio of non-freezable water in the partially hydrolyzed PVA is higher than 1.0 (Table 1) and increases with the vinyl acetate content. It seems thus that the vinyl acetate unit has a greater ability to interact with water in PVA than in pure PVAc.

In PVP, the average number of water molecules per C=O in the amide group is 4.2, as every C=O group can be directly linked to only two water molecules via hydrogen bounds. The high value of this number (4.2) indicates that the interactions of the C=O group with water is sufficiently high to keep the water molecules in the secondary layers in the non-freezable state.

The ion pair composed of a carboxylate anion on the polymer chains and a mobile counter cation is more or less dissociated in the presence of water. Both the ion pair and the dissociated ions have their own ability to attract water molecules, depending on their strength and their dissociation degree in the membrane. However, the dissociated ions always have larger hydration ability than the corresponding ion pair. The lowest hydration number for the Li membrane means that Li carboxylate is the most difficult pair to be dissociated by water. This behavior is consistent with the smallest radius of the bare Li$^+$ ion and the strongest electrostatic interaction due to its short distance from $-COO^-$, compared with the other cations.

3.3. Influence of polymer chemical structure on freezable bound water properties

When the water content in a hydrophilic polymer exceeds its characteristic threshold, the water quantity in excess of the non-freezable water can crystallize at a temperature lower than 0°C. In the DSC heating-sequence, the melting point of this freezable bound water increases linearly with the water content (Fig. 3).

The melting point data concerning the freezable-bound water in different PVA samples are shown in Table 2. When the water content in PVA with different hydrolysis degrees is maintained constant, the higher the hydrolysis degree (i.e. the hydroxyl content) the lower the freezable-bound water melting point. It appears that the lowering of the freezable bound water melting point is due to the increase in the overall hydrogen bonding ability of the polymer.

When the water content is maintained at ca. 42% in PE-*g*-AA films with different alkali metal counter-ions, the melting point of the freezable bound water decreases with the increase in the counter-ion atomic number. Again, this behavior can be explained by an increase in the overall hydrogen

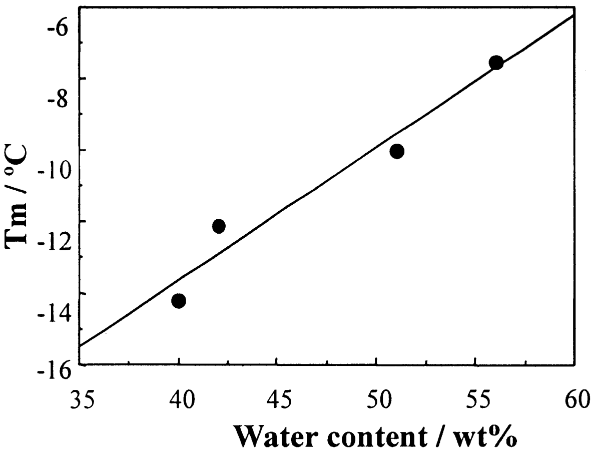


Fig. 3. Variation of melting point of freezable-bound water as a function of water content in PVA88.

Table 2
Variations of melting point of freezable bound water (T_{m_2}) with the polymer nature for the same water content in the polymer

Polymers	Film	Water (wt%)	T_{m_2} (°C)
PVA of different hydrolysis degrees	PVA88	40	−7.6
	PVA95		−14.2
	PVA100		−18.6
Polyethylene grafted acrylate (with different counter ions)	PE-*g*-AA$^-$K$^+$	42	−14.2
	PE-*g*-AA$^-$Na$^+$		−9.2
	PE-*g*-AA$^-$Li$^+$		−2.0

bonding ability due to the increased dissociation of the ion pairs in the films.

When the quantity of water in any polymer of both groups (Table 2) increases further, two endotherms of water melting are observed in the DSC thermograms (Fig. 4), one at ca. 0°C (the melting point of normal ice), and the other towards lower melting temperatures. The part of water molecules which melts at a temperature close to 0°C is assigned to bulk-like water, and that melting at lower temperatures is assigned to the freezable-bound water, as the latter peak is located in the line of the freezable-bound water observed at lower water contents. If the water content in the polymer increases further, the two peaks merge progressively to become a broad band at high swelling degrees. Such a broad endothermic peak was also observed in other hydrophilic polymers [19–23].

The quantity of bulk-like water depends greatly on the nature of the polymer matrix. If there are no physical or chemical crosslinks between polymer chains, a hydrophilic polymer can absorb more and more water when the external water activity increases, and ultimately dissolves in liquid water (water activity = 1). This is precisely the case for uncrosslinked PVP. In the case of PVA, the crystallites formed in the film casting process can prevent the materials from complete dissolution in water: the crystallites play thus the role of crosslinks in the polymer. PVA100 whose crystallinity degree is ca. 40% swells to a large extent in liquid water (absorbed water/dry polymer weight ratio of ca. 150%), while the same polymer prepared in such a way that the crystallinity degree is ca. 25% reaches this swelling ratio at a water activity of ca. 0.9. From these results, we infer that the quantity of freezable water in a hydrophilic polymer depends on the hydrogen bonding ability of the polymer polar groups. The higher the resistance of the matrix to a swelling action, the lower the total quantity of water (i.e. that of freezable water) absorbed in the polymer.

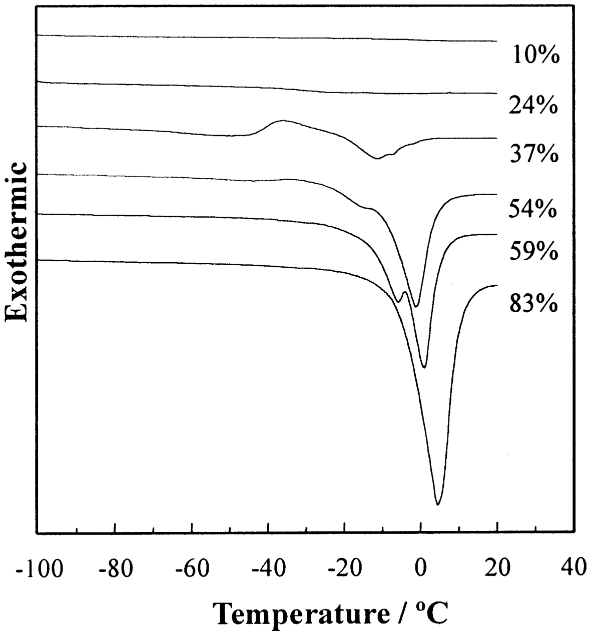


Fig. 4. DSC curve of the water absorbed in PVA88 with different water content; heating rate: 10 K min^{-1}.

3.4. Study of the interaction between various types of bound water and polymer polar sites by FTIR spectroscopy

The formation of hydrogen bond brings about a shift in the IR frequency of the acceptor group stretching vibration towards smaller values. For instance, the C=O stretching band in PE-*g*-AA$^-$M$^+$ shifts from 1558 to 1552 cm^{-1} when the polymer is swollen by water [24].

Zundel [25] proposed in an IR study of polystyrene-sulfonic membrane at different hydration degrees that the shoulder at 3250 cm^{-1} can be ascribed to the OH stretching vibration of the hydrogen bond of the water molecules of ‘type-I attachment’, and the intense band at 3430 cm^{-1} to those of ‘type-II attachment’, which correspond to the water molecules in the first and the second hydration layers of the polyelectrolyte, respectively.

We found that the OH stretching vibration band at ca. 3250 cm^{-1} in the PE-*g*-AA$^-$Li$^+$ membranes containing different water amounts is more intense when the water content in membrane is lower than 25% (Fig. 5). As it is generally accepted, the lowest wave number of the OH stretching band can be assigned to that of the water molecules of the strongest hydrogen bond with the carboxylate of the polymers, i.e. the water molecules in the first hydration layer. It means that the proportion of strongly bound water is higher at low water content in the membrane. However, the OH stretching band maximum shifts towards higher frequencies (ca. 3400 cm^{-1}) at high external relative humidity. One can infer that the water hydrogen bonds (on the average) are weakened due to the intercalation of non-freezable water from the polar sites of the polymer.

It should be emphasized that the cause of non-crystallizability of water molecules absorbed in a polymer should not be the same for hydrophilic polymers as for hydrophobic ones. For the latter, the part of non-freezable water is very small and corresponds to a random dispersion of the water

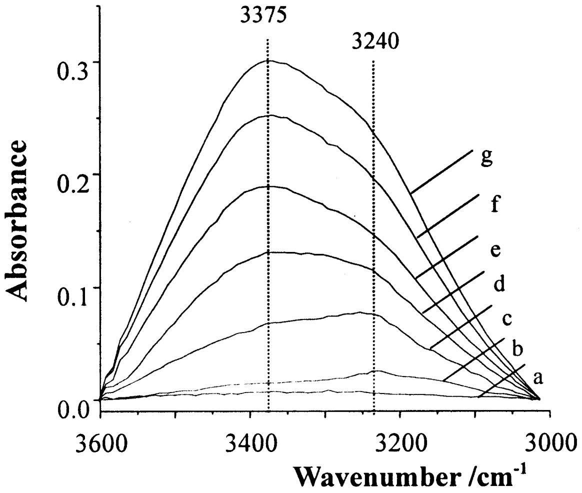


Fig. 5. Changes in the wave number of the hydroxyl stretching vibration in the PE-*g*-AA$^-$Li$^+$ membrane with the water content in the membrane; a: 0%, b: 5%, c: 17%, d: 31%, e: 48%, f: 54%, g: 64%.

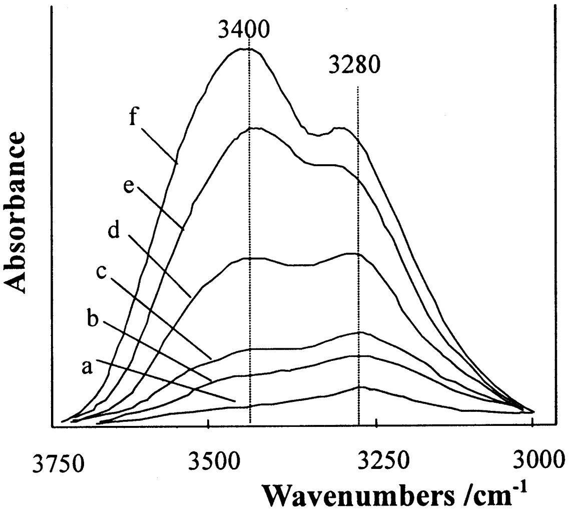


Fig. 6. Changes in the spectra of the PVA hydroxyl stretching vibration with the water content in the membrane; a: 4.2%, b: 6.3%, c: 10.2%, d: 19%, e: 40%, f: 59% (the spectra were obtained by subtracting the spectra of swelling membranes from that of the dry ones).

molecules (due to an entropy effect) throughout the entire polymer matrix. On the contrary, in hydrophilic polymers, water molecules are so strongly bound to specific polar sites by hydrogen bonds that they cannot gather with other molecules to form crystallizable water. The removal of water molecules from the sites would require a large driving force (chemical potential), which cannot be provided by the surrounding medium during cooling.

The OH stretching band of liquid water is very large, without shoulders, due to the existence of continuum of hydrogen bonds of different strengths. Although the alcohol hydroxyl stretching band in PVA is also large and is in the same frequency range, we were able to evidence its variation in frequency with increasing water contents in the polymer by subtracting the spectrum of the dry membrane to that of the swollen membranes (Fig. 6). One can see two distinct bands at fixed frequencies but with different intensities, depending on the water contents. The OH stretching band at 3280 cm^{-1} is more pronounced than that at 3400 cm^{-1} when the water content in membrane is lower than 20%. When the water content in PVA increases, the OH stretching band at 3400 cm^{-1} becomes more and more intense (Fig. 6). These two bands have approximately the same intensities at ca. 20 wt% of water in the polymer (Fig. 6). Thus, there are two distinct populations of water molecules, which are present at every water content level in the polymer. The non-freezable-water fraction in polymer systems of low water content includes then water molecules of the second hydration layer. However, there should also be a dynamic exchange of water molecules between sites and hydration layers. Apparently, these exchanges did not prevent the molecules from being under the polar-site interaction field, which kept the water molecules non-freezable. These results are also consistent with the high values of the average number of non-freezable water molecules per site (compared with that of hydrogen-bondable molecules) for PVP and for PE-*g*-AA salts (Table 1), where non-freezable water must consist of molecules coming from the second hydration layer.

4. Conclusion

Below a water content threshold whose value depends on the chemical and physical structures of the polymer, the water molecules absorbed in hydrophilic polymer cannot form ice crystals in the polymer matrix. Beyond this threshold, the absorbed water crystallizes at a temperature lower than the normal-water melting point, which increases with increasing water content in the polymer. Although the water molecules of this type are not directly attached to the polymer polar sites, their behavior is modified from that of bulk water.

We showed that the absorbed water in hydrophilic polymer develop two types of hydrogen bonds, one corresponds to water molecules directly attached to the active site of the polymer to form the first hydration layer, the second to water molecules in the second hydration layer. The latter are present in the polymer even at low water contents, i.e. the second hydration layer can be formed on certain sites before all polar sites are saturated with water molecules. This difference in the type of the water molecules bound to the polymer polar sites led to the observed changes in the behavior of the absorbed water in crystallization. The non-freezable water did not consist exclusively of water molecules from the first hydration layer.

The different states of water in hydrophilic polymers reflect the power of the interactions between the absorbed molecules and the polymer sites. The influence of these intermolecular interactions is general, therefore should be taken into account whenever a polymer is used in the presence of a solvent.

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