D.s.c. investigation of the states of water in poly(vinyl alcohol) membranes

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D.s.c. analysis shows that heat absorbed in the heating process of water in poly(vinyl alcohol) membranes is higher than that evolved in the cooling process. A remarkable discrepancy is found between these heats when the water retention, H, of the membrane is lower than 0.5 g H_2O/g swollen membrane. The amounts of freezable water in the membranes were estimated by use of the relation observed between the temperature and the enthalpy of the crystallization of super-cooled water. The amounts estimated from the heats absorbed or evolved agree within 2% when H was above 0.6. When H is below 0.5, however, the ratio of these two amounts was greater than 2. This difference is explained by the heat capacity of the water below 250 K increasing anomalously compared with that of bulk water.

INTRODUCTION

D.s.c. analysis is often used to estimate the amounts of free, freezable bound and nonfreezing water in water-swollen membranes. Free water is defined as the water which has the same phase transition temperature as bulk water[1]. Freezable bound water is the water having a phase transition temperature lower than 273 K. This depression is usually ascribed to the weak interaction of the water with the polymer chain of the membrane[2] and/or the capillary condensation in the membranes[3,4]. Nonfreezing water is defined as the water which has no detectable phase transition from 273 to 200 K[5]. The water is supposed to be influenced by the strong interaction with the polar moieties of the polymer chain.

In most investigations[1-3,6] the melting enthalpy of water at 273 K has been used to calculate the amount of freezable bound water in membranes, although the transition temperature is clearly lowered[7,8]. For supercooled bulk water, the crystallization enthalpy, $\Delta H(T)$, is known to be lower than that of bulk water at 273 K[9], as expressed by:

$$\Delta H(T) = \Delta H(273) - \int_{T}^{273} \Delta C_p dT \qquad (1)$$

where ΔC_p is the difference of heat capacities of ice and supercooled water. The same relation may be applied to the freezable bound water.

In our previous study[5] the states of water in gel cellophane membranes (water retention, $H = 0.769$ g H_2O/g swollen membrane) were investigated at cooling and heating rates of 0.31–10 K min^{-1} by d.s.c. measurements. An exothermic peak was observed between two endothermic peaks in the d.s.c. heating curves when the heating rate was less than 2.5 K min^{-1}. Heats absorbed in the heating process accord with those evolved in the cooling process within the experimental error[5]. The amounts of water were estimated by using the phase transition enthalpy of the bulk water at 273 K. In the present work the d.s.c. analysis of water-swollen

poly(vinyl alcohol) (PVA) membranes was performed in both cooling and heating processes. It is observed that the heat absorbed in the heating process is 9% higher than that evolved in the cooling process at $H > 0.6$. The accuracy of detecting heats was improved by using the larger amounts (~ 8 mg) of samples compared with ~ 2 mg in the previous work[5]. A remarkable discrepancy is, however, found between these heats at $H < 0.5$. The amounts of freezable water in the membranes were estimated by use of the relation observed between temperature and the enthalpy of crystallization of super-cooled water. The assumption used in the estimation is carefully discussed.

EXPERIMENTAL

Materials

PVA supplied by Nakarai Co. Ltd. (degree of hydrolysis $> 99\%$, molecular weight 88 000) was used after Soxhlet extraction with methanol for 12 h. Deionized and distilled water was used throughout the experiment.

Membrane preparation

PVA aqueous solution (10%) was stirred at 100°C for 4 h to dissolve completely and subsequently kept at 21°C for 48 h to insure that no air bubbles were present in the solution. PVA membranes were prepared by casting the aqueous solution on clean glass plates and drying at $21° \pm 2°$C for a week.

For crosslinking the membranes were immersed in an aqueous solution of 20% Na_2SO_4, 1% H_2SO_4, 0.1% glutaraldehyde at $25° \pm 0.02°$C after being swollen in an aqueous Na_2SO_4 solution. The characteristics of the membranes thus prepared are listed in *Table 1* together with the immersion time (I.T.). The thickness of the water-swollen membrane was between 400 and 600 μm.

D.s.c. measurements

External surface water was removed from the membranes by blotting with filter paper. About 8 mg of the membranes were sealed in aluminium pans which had been pretreated in boiling water for 1 h. D.s.c. measure-

Table 1 Characteristics and phase transition temperatures of water-swollen PVA membranes

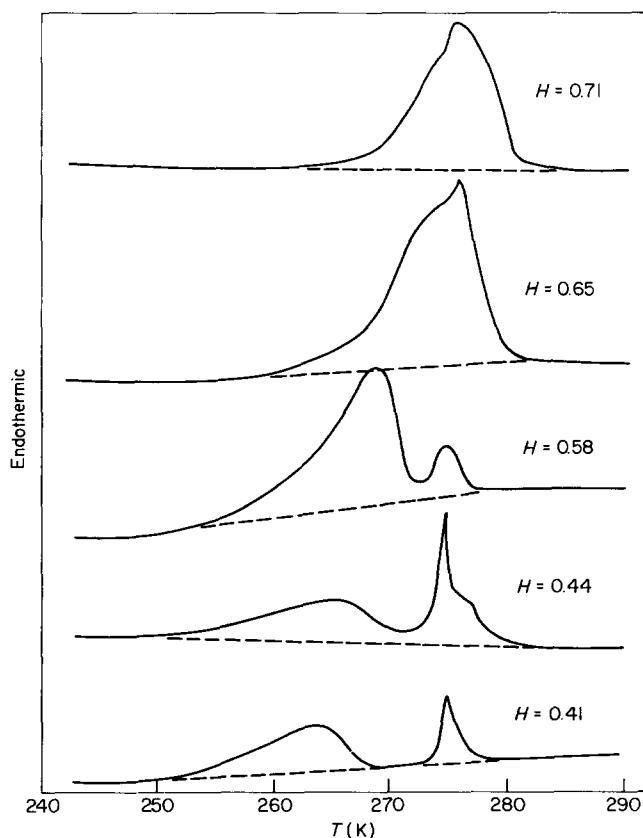| Sample	H	T_1^h	T_2^h	T_1^c	T_2^c	I.T. (h)
VA-85	0.85	—	270	$252._2$	—	0.5
VA-71	0.71	273	$267._7$	$252._5$	—	2
VA-68	0.68	273	$267._5$	$253._8$	—	3
VA-65	0.65	273	$267._3$	255	—	4
VA-58	0.58	273	264	$254._8$	—	8
VA-46	0.46	273	256	255	234	24
VA-44	0.44	273	252	254	229	96
VA-41	0.41	273	250	$256._5$	$229._5$	168

— No peak was observed in the d.s.c. curve

Figure 1 D.s.c. heating curves of water-swollen PVA membranes. Heating rate $= 10\,K\,min^{-1}$

ments of the sealed samples were performed by cooling from 320 to 200 K at the rates of 10, 5, 2.5 and $1.25\,K\,min^{-1}$ and subsequent heating to 320 K at the same rates. The errors of phase transition temperature and heat detections are within $\pm 0.5\,K$ and $\pm 5\%$.

RESULTS AND DISCUSSION

D.s.c. heating curves of water-swollen PVA membranes at a heating rate of $10\,K\,min^{-1}$ are shown in *Figure 1*. With the decrease of water retention of membranes, the peak around 273 K was found to be separated into two peaks. This indicates that there are at least two states of freezable water in the membranes, i.e. free water and freezable bound water, which we denote Peak 1^h and Peak 2^h. The two peaks were observed to be more clearly separated at a heating rate of $1.25\,K\,min^{-1}$ than at that of $10\,K\,min^{-1}$ (i.e. *Figure 4*) except for VA-85. *Table 1* gives the phase

transition temperatures for Peak 1^h and Peak 2^h observed in the heating process (T_1^h and T_2^h), which were determined on the curves at a heating rate of $1.25\,K\,min^{-1}$. T_1^h for all the membranes except VA-85 appears at the same 273 K, within the experimental error. VA-85 of the highest water retention in this study gave only one endothermic peak in the heating process. T_2^h, 270 K, of this membrane is thought to be too close to T_1^h to give separate peaks.

Figure 2 shows d.s.c. cooling curves of membranes at a cooling rate of $10\,K\,min^{-1}$. In contrast to d.s.c. heating curves single exothermic peaks (Peak 1^c) due to the crystallization are observed near 255 K for membranes of $H \geqslant 0.58$. Bulk water crystallized also near 255 K under the same cooling condition. Another exothermic peak near 230 K (Peak 2^c) is observed for membranes of $H < 0.5$. Crystallization temperatures for Peak 1^c and Peak 2^c (T_1^c and T_2^c) are summarized in *Table 1*. Peak 2^c appears only when T_2^h becomes close to T_1^c.

VA-58 membrane was cooled to 250 K just before starting the crystallization and was kept at the same temperature for 30 min. The exothermic peak observed during the time of the duration was exactly the same as that observed for the normal cooling experiments to 200 K. The broad peak of VA-58 is not due to the wide distribution of the crystallization temperatures but the existence of water phases which crystallized with different rates of nucleation. The two states of water observed in the heating process must be included in the single exothermic peak for the membranes of $H \geqslant 0.58$ in the cooling process.

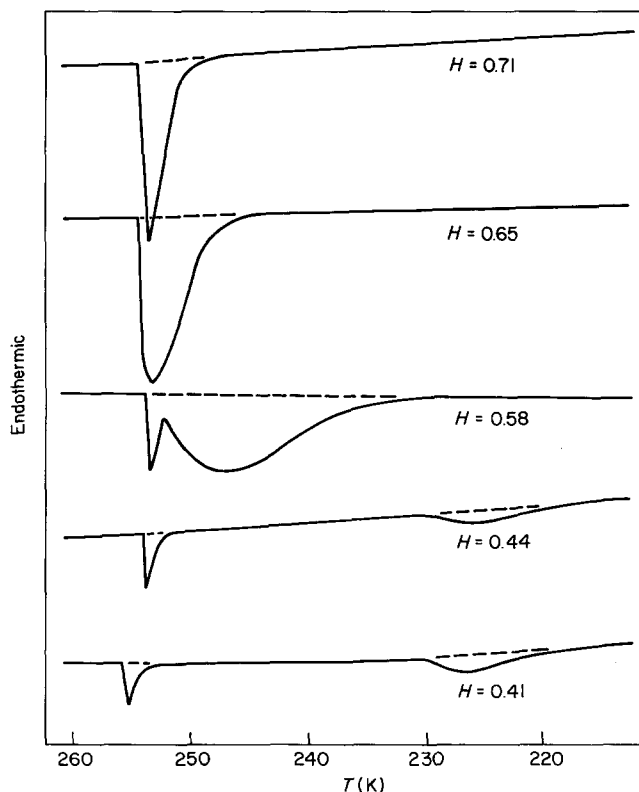For the membranes of $H \leqslant 0.46$, two peaks are observed in the cooling process. The following two experimental

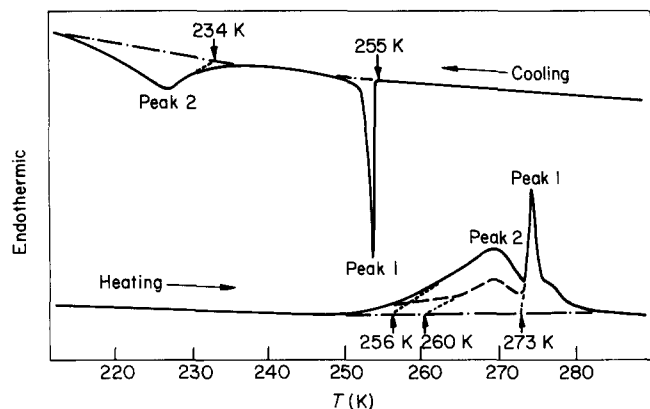**Figure 2** D.s.c. cooling curves of water-swollen PVA membranes. Cooling rate $= 10\,K\,min^{-1}$

Figure 3 D.s.c. curves of water-swollen PVA membrane in heating and cooling processes. $H = 0.46$. (———) Cooled to 200 K; (———) cooled to 250 K
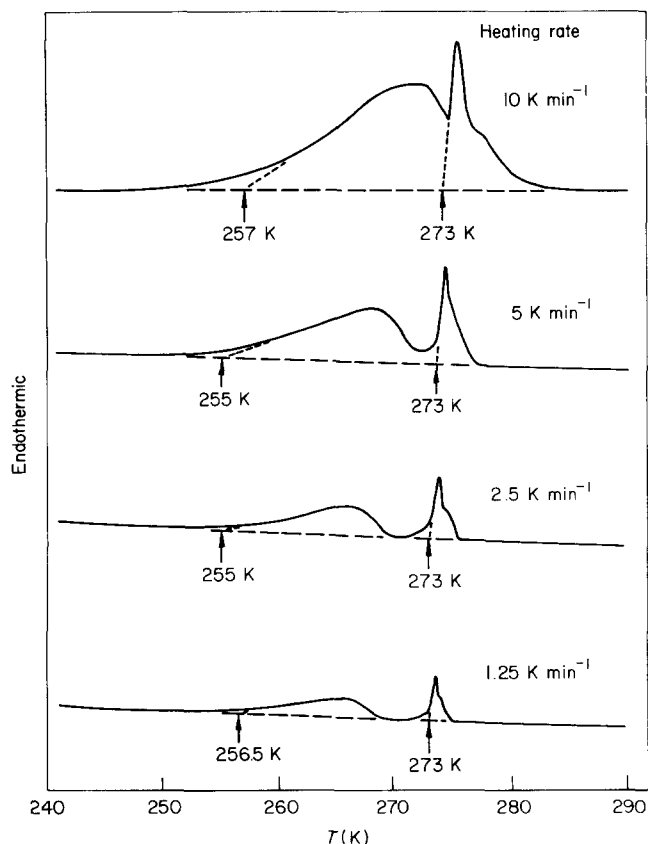

Figure 4 Heating rate dependence of d.s.c. curves of water-swollen PVA membranes and their transition temperature. $H = 0.48$

Figure 4 shows the dependence of d.s.c. heating curves on the heating rates (10, 5, 2.5 and 1.25 K min⁻¹) for the membrane of $H = 0.48$. The melting temperature of Peak 1ʰ is found at 273 K irrespective of the heating rate. Although Peak 2ʰ curves are broad, the melting temperatures are at 256 ± 1 K also independent of the heating rate. T_1^h and T_2^h in *Table 1* are those determined on the curves obtained at 1.25 K min⁻¹.

Figure 5 shows the dependence of the ratio of heats absorbed in the heating and cooling processes $-Q_T^h/Q_T^c$ on the water retention. $-Q_T^h/Q_T^c$ was found to be constant, 1.09, for the membranes of $H > 0.6$. However, with the decrease of water retention below $H < 0.6$, the discrepancy between Q_T^h and $-Q_T^c$ becomes remarkable. If the same heat of fusion is used, the amount of the freezable water calculated for the cooling process is different from that for the heating process. This implies that the temperature dependency of its heat of fusion must be taken into consideration. The amounts of water calculated in the cooling process (W^c) can be compared with those obtained in the heating process (W^h) by assuming that the relationship of equation (1) is applied to the water in the membrane. ΔC_p were calculated by the heat capacity of ice[10] and supercooled water[9]. The results obtained are summarized in *Table 2*. The agreement between W^h and W^c at $H > 0.6$ is found to be fairly good yielding the value of 0.98 for the average ratios of W^h and W^c at $H > 0.6$. There still remains, however, the discrepancy between W^h and W^c at $H < 0.6$. A ratio of W^h to W^c of more than 2 is observed at $H = 0.46$, 0.44 and 0.41. Those membranes have Peak 2ᶜ near 230 K. Therefore, the discrepancy can be ascribed to the incorrect estimation of enthalpy for Peak 2ᶜ in use of equation (1).

The weight of freezable water in membranes can be calculated by equations (2) and (3).

$$W^h = \sum_n (Q_n^h/\Delta H_n^h) \tag{2}$$

$$W^c = -\sum_n (Q_n^c/\Delta H_n^c) \tag{3}$$

where Q_n^h and Q_n^c are the transition heats determined experimentally, corresponding to n state of water in heating and cooling processes. ΔH_n^h and ΔH_n^c are enthalpies for the phase transition in heating and cool-

results indicate that water for Peak 2ᶜ corresponds to a part of water for Peak 2ʰ in the heating process. D.s.c. cooling and heating curves obtained in two procedures are shown in *Figure 3*. In the first procedure the sample was cooled from 320 to 200 K with the rate of 10 K min⁻¹ and then heated back to 320 K at the same rate. In the other procedure the sample was cooled at the same rate from 320 to 250 K, being kept at 250 K for 10 min and then the sample was heated back to 320 K at the same rate. Peak area and phase transition temperature of Peak 1ʰ in the former procedure was found to be the same as those in the latter procedure. Peak 2ʰ area in the latter procedure was about one half and the T_2^h shifted from 256 to 260 K (see *Figure 3*). As the water for Peak 2ᶜ is still in liquid state at 250 K, the water for Peak 2ᶜ seems to contribute solely to Peak 2ʰ in the heating process.
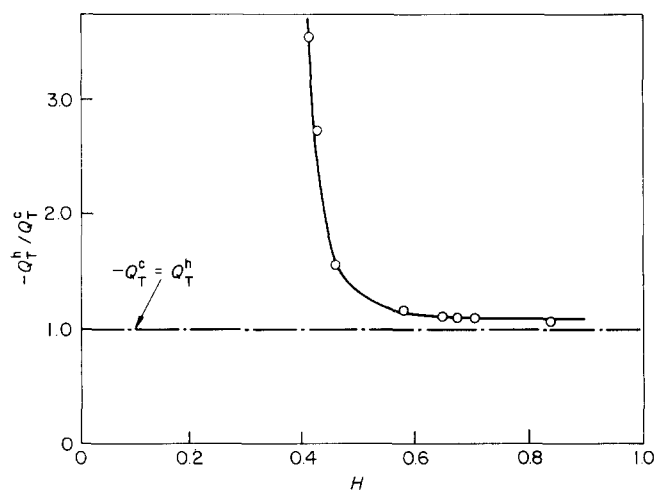

Figure 5 Relation between $-Q_T^h/Q_T^c$ and water retention of water-swollen PVA membranes

Table 2 Q_T^h/Q_T^c and W^h/W^c calculated by equations (1) and (6) for water-swollen PVA membranes

Sample	H	Q_T^h/Q_T^c	W^h/W^c (by equation (1))	W^h/W^{c*} (by equation (6))	$W^h/W^{c\dagger}$ (by equation (6))	$W^h/W^{c\ddagger}$ (by equation (6))
VA-85	0.85	1.07	0.94			
VA-71	0.71	1.12	1.00			
VA-68	0.68	1.09	0.99			
VA-65	0.65	1.09	1.00			
VA-58	0.58	1.15	1.06			
VA-46	0.46	1.54	2.56	0.79	1.02	0.97
VA-44	0.44	2.56	1.99	1.10	0.85	0.91
VA-41	0.41	3.59	2.75	1.34	1.15	1.19

* Calculated by $l=1$ in equation (6)
† Calculated by $l=2$ in equation (6)
‡ Calculated by $l=3$ in equation (6)

ing processes, which are combined with each other by equation (4).

$$\Delta H_n^c = \Delta H_n^h - \int \Delta C_p(n) dT \qquad (4)$$

where $\Delta C_p(n)$ is the difference in heat capacity of n state of water and ice in the membrane. Then equation (5) should be satisfied.

$$W^h = W^c \qquad (5)$$

The estimation of ΔH_n^h, ΔH_n^c and $\Delta C_p(n)$ for all states except free water is difficult. It may be reasonable to assume that the heat of fusion of water in the membrane above 250 K obeys equation (1) for the bulk water, because a good agreement of W^h with W^c at $H > 0.6$ is found, and all the phase transitions (T_1^h, T_2^h, T_1^c and T_2^c) are observed above 250 K (see *Table 1*). The discrepancy between W^h and W^c at $H < 0.6$ may be attributed to the inadequate estimation of the enthalpy of the membrane water by means of equation (1) below 250 K. Assuming that equation (1) holds above 250 K, it is possible to estimate the enthalpy of the water in the membrane below 250 K by equations (2)–(6).

$$\Delta H = \Delta H(250) - \int\limits_T^{250} \Delta C_p(n) dT \qquad (T < 250 \text{ K})$$
$$\qquad (6)$$

$$\int\limits_T^{250} \Delta C_p(n) = \sum_{m=0}^{m=l} a(m) T^m \qquad (l \geq 1)$$

where $a(m)$ is a parameter which is determined to satisfy equation (5) by least square method. W^h/W^c obtained by using equation (6) on the condition of $l=1, 2$ and 3 are also summarized in *Table 2*. W^h/W^c thus obtained shows satisfactory agreement within 15% deviation for $l=2$. It is also found that there is no essential difference of W^h/W^c for different l values. ΔH estimated by equation (6) is 46.3 ($l=2$) and 43.2 ($l=3$) mcal mg^{-1} at 235 K, while ΔH calculated by equation (1) is 53.2 mcal mg^{-1}. It is considered that the freezable bound water which corresponds to Peak 2^c is strongly bound to OH groups of nonfreezing water and polymer matrix, and will cause the large deviation of ΔH in the membrane from that of the bulk water.

The large discrepancy in Q_T^h and $-Q_T^c$ can be ascribed to the large difference between ΔH^h and ΔH^c. It can be further expected that ΔC_p in the membrane is much larger than ΔC_p of the bulk water below 250 K. *Figure 6* shows heat capacity of ice, supercooled bulk water and water in the membrane. The heat capacity of water in the membrane is obtained by differentiating equation (6). The heat capacity of bulk water shows an anomalous rise below $-20°C$, as already discussed by Angell and Tucker[11] and reviewed elsewhere[12]. The heat capacity of water in the membrane estimated in the present study reveals more striking rise than that of the bulk water below 250 K. It
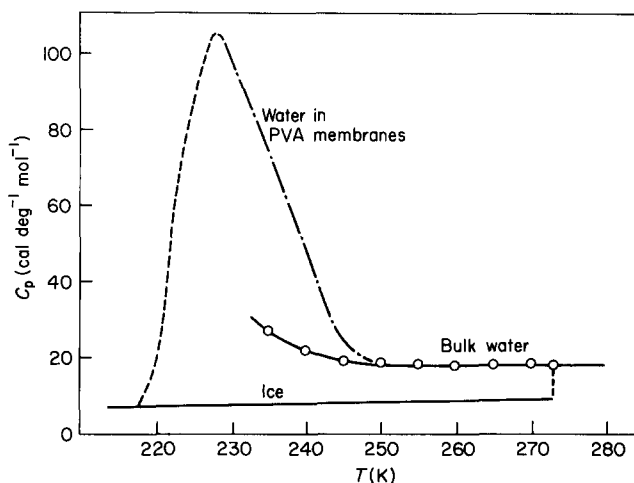

Figure 6 Heat capacity (C_p) of bulk water, ice and water in water-swollen PVA membranes as a function of temperature
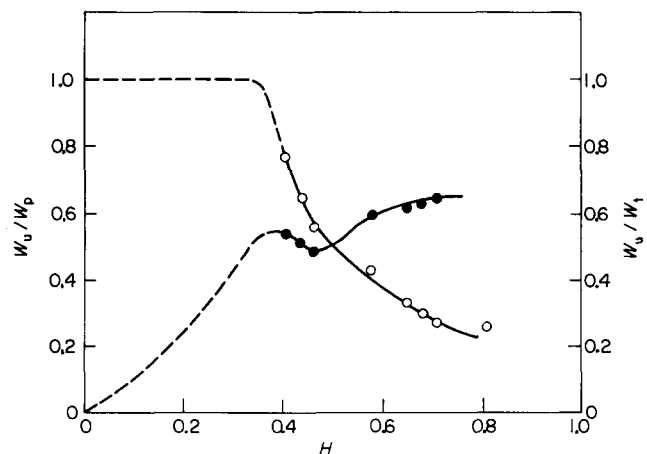

Figure 7 Weight ratios of unfrozen water (W_u) to total water (W_t) and to dry polymer (W_p) in water-swollen PVA membranes

was reported by several investigators[3,13] that heat capacity (C_p) of water in membranes was higher than that of the bulk water. It is not easy to see the reason for the anomalous rise of heat capacity of the water in the membrane below 250 K, since water in the membrane crystallizes in a heterogeneous nucleation mode, and the expansivity (α), compressivity (κ) and constant volume heat capacity (C_v) of the bound water have not yet been obtained. The striking rise of the C_p of water in the membrane may be due to larger value of α and/or smaller value of κ compared to that of the bulk water, as suggested by Angell and Tucker[11] for the anomalous heat capacity rises (C_p) of bulk water.

Unfrozen water content in the membrane is determined by subtracting the freezable water which has been discussed above from the total water. The weight ratios of unfrozen water (W_u) to total water (W_t) (W_u/W_t) and to polymer (W_u/W_p) are shown in *Figure 7*. W_u increases with decrease of the water retention. All the water in the membranes of $H \leqslant 0.35$ will be unfrozen. W_u/W_p showed a minimum at the membrane of $H = 0.46$. It is difficult to give an explicit answer for the minimum, although it may be due to the existence of freezing water which can not crystallize above 200 K that is the lowest temperature achieved in this study. The weight of unfrozen water calculated in this study may be, therefore, overestimated

than the real value at $H = 0.41$ and 0.44. This is consistent with the shift of Peak 2^c to lower temperature as shown in *Figure 2*, since a part of bound water in Peak 2^c is expected to shift below 200 K.

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