D.s.c. investigation of the states of water in poly(vinyl alcohol–co-itaconic acid) membranes

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The state of water in water-swollen poly(vinyl alcohol–co-itaconic acid) membranes, having various water contents from 0.31 to 0.83, was investigated by d.s.c. measurements and compared with those in water-swollen poly(vinyl alcohol) membranes. The amount of freezing water in the membranes was estimated by use of a relationship between the phase transition temperature and the enthalpy of the crystallization of supercooled water. The melting temperature of the water in the membranes immersed in urea and NaCl 0–$2 \, \text{mol} \, l^{-1}$ aqueous solutions was also determined by d.s.c. analysis. The present study proposes a method for estimating the solubilities of urea and NaCl in both of the freezing and the non-freezing water using the melting point depression of the freezing water in the membranes immersed in the solute solution.

(Keywords: water; membrane; poly(vinyl alcohol–co-itaconic acid); differential scanning calorimetry; solubility; sorption; urea; sodium chloride)

INTRODUCTION

The melting temperature of the freezable bound water[1-4] in membranes is frequently observed between 270–250 K and the depression is commonly ascribed to a weak interaction of the water with the network polymer chain[4] and/or capillary condensation in the membranes[5,6]. The assumption that the heat of fusion of water in the membranes is identical to that of pure bulk ice (79.4 cal/g) is, therefore, erroneous[1]. The heat of fusion in the membranes must be substantially lower than that of pure bulk ice, while it was often used[2-5,7] to calculate the amounts of water in the membranes. Frommer *et al.*[8] and our previous study[1] suggested that a lowering of the heat of fusion resulted from the difference in heat capacity between the pure bulk water and the water in the membranes.

In the previous study[1], d.s.c. analysis of water-swollen poly(vinyl alcohol) membranes $(0.41 \leqslant$ water content $\leqslant 0.85)$ was performed in cooling and heating processes. A remarkable discrepancy was found between heat absorbed in the heating process and that evolved in the cooling process at water contents below 0.5 g of water/g of swollen membrane. This discrepancy was attributed to the anomalous increase of the heat capacity of the water in the membranes below 250 K. The total amounts of freezing (freezable) water (i.e., free water and freezable bound water) in the membranes were estimated by use of the relation observed between the melting temperature and the enthalpy of the crystallization of supercooled water as shown by equation (1).

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

where ΔC_p is the difference of heat capacities of pure bulk ice and pure supercooled water and ΔH is the heat of fusion. In the present investigation, the d.s.c. analysis of water-swollen poly(vinyl alcohol–co-itaconic acid) (PVA–IA) membranes $(0.31 \leqslant$ water content $\leqslant 0.83)$ was performed and compared with that of the previous work[1] on water-swollen poly(vinyl alcohol) (PVA) membranes. The melting temperature of water in PVA–IA membranes immersed in 0–$2 \, \text{mol} \, l^{-1}$ urea and NaCl aqueous solutions was also determined by d.s.c. analysis. The present study suggests that the solubilities of urea and NaCl in the freezing water of the membranes can be estimated from the melting point depression[9] of the water in the membranes. The solubilities in the non-freezing water were further estimated using a desorption method[10,11] and compared with those in the freezing water.

EXPERIMENTAL

Poly(vinyl alcohol–co-itaconic acid) (PVA–IA) with $1.3 \, \text{mol}\%$ itaconic acid, a degree of hydrolysis of $97.7 \, \text{mol}\%$ and a degree of polymerization of 1750 was kindly supplied by Kuraray Co. Ltd. PVA–IA was purified by Soxhlet extraction with methanol for 12 h before use. Distilled water, from deionized water, was used throughout the experiments. NaCl and urea, of special reagent grade purchased from Nakarai Chemicals, Ltd., were used in this study. The previous method[1,12] of membrane preparation and crosslinking with glutaraldehyde was performed here. D.s.c. measurement procedures were also described in the previous papers[1,13]. D.s.c. measurements of the sealed samples were performed by cooling from 320 K to 200 K at the rates of 10 and 1.25 K/min followed by heating to 320 K at the same rates.

RESULTS AND DISCUSSION

Water-swollen PVA–IA membranes

Figure 1 shows the d.s.c. heating curves of water-swollen PVA–IA membranes at a heating rate of 10 K min^{-1}. The overlapped peaks at approximately 273 K were found to be separated into two peaks with the decrease in water content of the membranes at $H \geqslant 0.49$. This suggests that there are at least two states of freezing water (i.e., free water and freezable bound water) in the membranes, which are assigned to peak 1^h and peak 2^h on the d.s.c. curves, respectively. *Table 1* gives the phase transition temperatures of the water for peak 1^h and peak 2^h observed in the heating process (T_1^h and T_2^h, respectively) at a heating rate of 1.25 K/min. VI-83 having a water content of 0.83, the highest in this study, gave only one phase transition temperature, 270 K, in the heating
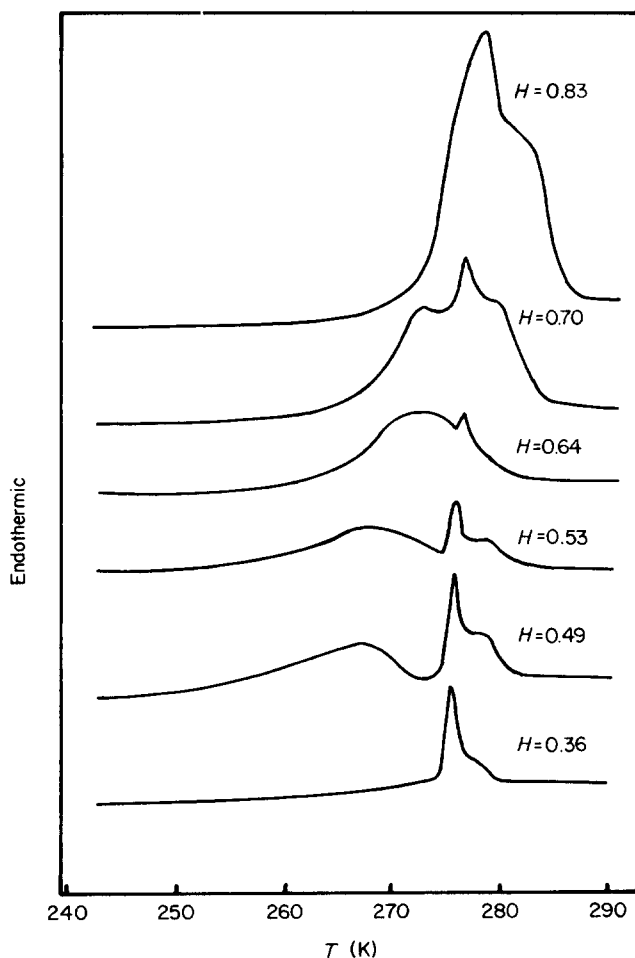

Figure 1   D.s.c. heating curves of water-swollen PVA–IA membranes, heating rate = 10 K/min

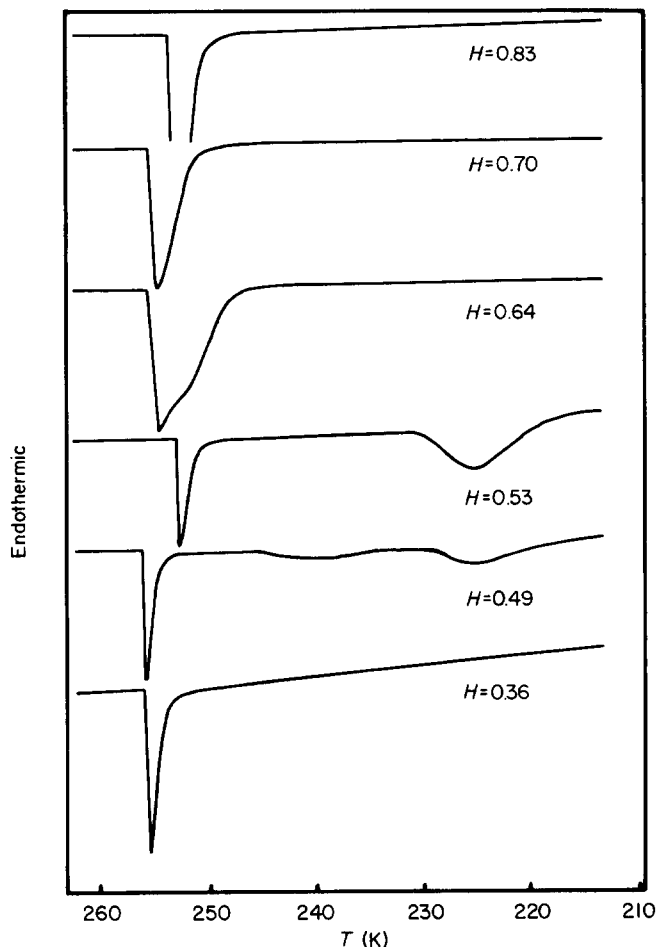**Figure 2**   D.s.c. cooling curves of water-swollen PVA–IA membranes, cooling rate = 10 K/min

process. This may be due to the closeness of T_1^h and T_2^h. This was also observed in the d.s.c. heating curves of water-swollen PVA membranes[1]. It is observed, however, that the peak for VI-36, having the lowest water content in this study, gave only a single endothermic peak as shown in *Figure 1*.

Figure 2 shows the d.s.c. cooling curves of the membranes at a cooling rate of 10 K/min. A single exothermic peak (peak 1^c) is observed at $H \geqslant 0.64$ in contrast to the heating curves. The broad peak of VI-64 is not due to the wide distribution of the crystallization temperatures but to the existence of water phases crystallized with a slow nucleation, since exactly the same peak shapes are observed at either cooling rates of 1.25 and 10 K/min. The crystallization temperatures of peak 1^c (T_1^c) and pure bulk water are found at approximately 255 K. The depression of the temperatures is due to the supercooling of the water. Other exothermic peaks below 255 K (peak 2^c and peak 3^c) are observed for the membranes with $0.4 < H < 0.6$. The crystallization temperatures of peak 1^c, peak 2^c and peak 3^c are also given in *Table 1*. Two exothermic peaks were also reported at $H < 0.5$ in the water-swollen PVA membranes[1]. The d.s.c. cooling curve for VI-36 is, however, found to give a single peak, peak 1^c, as is observed with VI-83. No peaks are observed for the membranes with $H < 0.3$. The above results may be interpreted as follows.

(1) The freezable bound water of the membranes having $H \geqslant 0.6$ crystallizes together with the free water at T_1^c as T_2^h was found to be above T_1^c. A slight degree of

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

Sample	H	T_1^h	T_2^h	T_1^c	T_2^c	T_3^c
VI-83	0.83	–	269.8	253.5	–	–
VI-70	0.70	273	268	255.5	–	–
VI-68	0.68	273	267	253	–	–
VI-64	0.64	273	266	255.5	–	–
VI-53	0.53	273	248	253	230	–
VI-49	0.49	273	253.5	255.5	244	229
VI-36	0.36	273	–	255.5	–	–
VI-31	0.31	–	–	–	–	–

–: no peak was observed in the d.s.c. curve

supercooling of the freezable bound water gives a slow nucleation of the water and leads to a broader peak in the d.s.c. cooling curves compared with the pure bulk water.

(2) The freezable bound water of the membranes having $0.4 < H < 0.6$ does not crystallize at $T_1{}^c$ but instead at $T_2{}^c$, since the melting temperature of the water $(T_2{}^h)$ was observed to be lower than $T_1{}^c$.

(3) Peaks 2^c and 3^c were not observed for the VI-36 membrane suggesting that the freezable bound water in this membrane may exist in a liquid state throughout the experiments above 200 K. In this way only the peak of free water was found in the d.s.c. cooling curves.

(4) $T_2{}^h$ of VI-49 is higher than that of VI-53 (see *Table 1*), although the water content of the former is lower than that of the latter. $T_2{}^h$ of the water-swollen PVA membranes was reported[1] to shift to the lower temperature with the decrease in the water content. This implies that only a part of the freezable bound water of VI-49 crystallizes at $T_2{}^c$ and the other part does not crystallize even at 200 K.

(5) No peaks for VI-31 were observed suggesting that the water in the membrane is non-freezing water or that the crystallization temperature of the freezable bound water is below 200 K. It would be interesting to investigate whether the non-freezing water reported in several studies[1–5,7,14] does not really have a phase transition temperature or has an extremely low transition temperature. Regrettably in this work we cannot give an explicit answer to this question since available d.s.c. equipment cannot be generally used at extremely low temperatures (i.e., below 150 K).

Figure 3 shows the relation between the ratio of heats observed in the heating and cooling processes, $-Q_T{}^h/Q_T{}^c$ and the water content of PVA–IA membranes. For comparison purposes the results for the PVA membranes[1] are also plotted in the same figure. $-Q_T{}^h/Q_T{}^c$ was found to have a constant value, 1.1, for both membranes having $H > 0.6$. The maximum was observed for PVA–IA membranes, while $-Q_T{}^h/Q_T{}^c$ increased monotonously with the decreasing water content of the PVA membranes. The discrepancy between $Q_T{}^h$ and $-Q_T{}^c$ is due to the presence of peaks 2^c and 3^c which have phase transition temperatures lower than $T_1{}^c$. Since peak 2^c was observed for all PVA membranes below $H < 0.6$, the discrepancy increased with decreased water content. VI-36 did not

give peak 2^c, therefore $-Q_T{}^h/Q_T{}^c$ for VI-36 was found to be close to unity. The above results suggest that an electrostatic interaction of the carboxyl groups with the water dipole in PVA–IA membranes leads the phase transition temperature of the freezable bound water to be lower than 200 K at $H < 0.36$.

The weight of freezable water, W_f, in the membranes can be estimated using equation (2)[1].

$$W_f = \sum_n Q_n{}^h / \Delta H_n{}^h \qquad (2)$$

where $Q_n{}^h$ is the heat absorbed in calories observed in the heating process and subscript n denotes the n state of water. $\Delta H_n{}^h$ is the heat of fusion calculated at various temperatures by equation (1) and is given in *Table 2*.

It is possible to estimate the weight of freezing water from the heats absorbed in both the heating and cooling processes. The weight of freezing water is, however, estimated only from the heating process in this study as it was reported[1] that the ΔHs of the water for peaks 2^c and 3^c are significantly different compared with the ΔH calculated by equation (1). This gives a significant discrepancy between $Q_T{}^h$ and $-Q_T{}^c$, and the maximum for PVA–IA or a monotonous increase for PVA membranes at $H < 0.6$ (*Figure 3*).

The weight of nonfreezing water can be calculated by subtracting the weight of freezing water estimated by equation (2) from the total weight of water. The weight ratios of non-freezing water (W_n) to the total water (W_t) in the membrane (W_n/W_t) and to dry polymer (W_n/W_p) are shown in *Figure 4*. It is found in the Figure that the ratio of non-freezing water to total water increases with a decrease
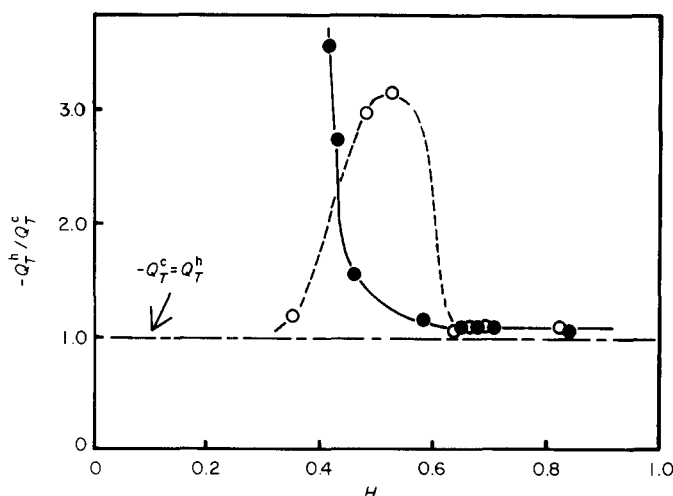
Table 2 Relation between phase transition temperature of water and its enthalpy calculated by equation (1)

T	ΔT	T	ΔH	T	ΔH	T	ΔH
273	79.4	267	76.4	261	73.3	255	70.1
272	78.9	266	75.9	260	72.7	254	69.5
271	78.4	265	75.3	259	72.2	253	68.9
270	77.9	264	74.8	258	71.7	252	68.3
269	77.4	263	74.3	257	71.2	251	67.7
268	76.9	262	73.8	256	70.6	250	67.0

Figure 3 Relation between $-Q_T{}^h/Q_T{}^c$ and water retention of water-swollen PVA (–●–) and PVA–IA (–○–) membranes
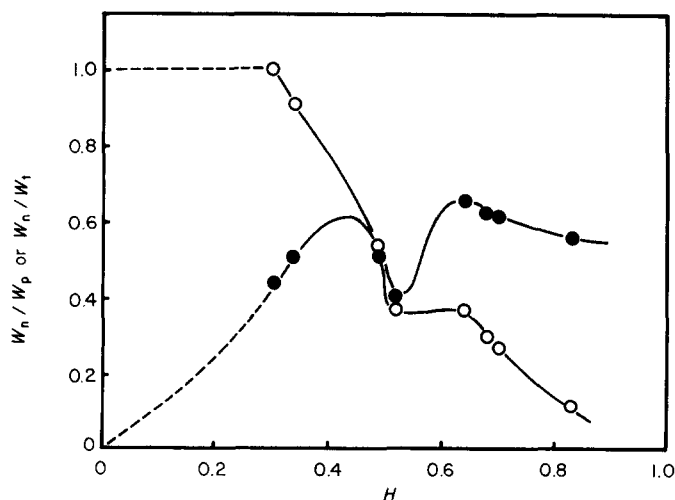

Figure 4 Weight ratios of non-freezing water (W_n) to total water (W_t) (–○–) and to dry polymer (W_p) (–●–) in water-swollen PVA–IA membranes

in the water content. The membrane with $H = 0.3$ is expected to have solely the non-freezing water. It is observed that W_n/W_p shows a minimum at $H = 0.53$. The corresponding membrane VI-53 has peak 2^c. It may be due to the fact that the freezing water of VI-53 is overestimated compared with the real value as was argued in the previous study on PVA membranes[1] where W_n/W_p showed a minimum at $H = 0.46$. VI-53 may have peak 3^c below 200 K. When the water for peak 2^c crystallizes, the water for peak 3^c may crystallize together with the water for peak 2^c with less supercooling. Peak 2^h observed in VI-53 may be, therefore, an overlapped peak with peak 3^h on the d.s.c. heating curves.

PVA–IA membranes immersed in aqueous solution of urea and NaCl

0–2 mol l^{-1} of aqueous urea and NaCl solutions were investigated using d.s.c. analysis, before the PVA–IA membranes immersed in the same aqueous solution were measured. D.s.c. heating curves of pure water, 2 mol l^{-1} aqueous urea and NaCl solution at a heating rate of 1.25 K/min are shown in *Figure 5*. It was observed that both the urea and the NaCl solutions have two peaks and the melt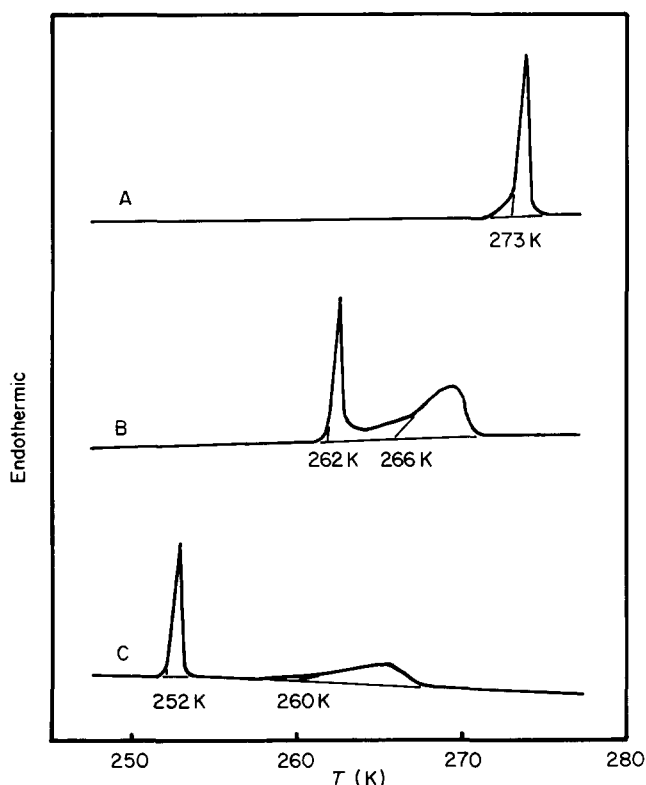ing temperatures are below 273 K, while the peak for the pure water is found to have a sharp single peak at 273 K. Two peaks are also observed for the urea and NaCl solutions in the cooling process. When NaCl or urea solution cooled from 300 K to 250 K (>200 K) is afterwards heated to 320 K, only a single peak (peak 1^c or peak 1^h) was observed in each of the cooling and heating processes. This indicates that the water for peak 1^c corresponds to that for peak 1^h and the water for peak 2^c is that for peak 2^h. Melting temperature of the urea solution is given in *Table 3*. It was observed that peak 1^h gradually became broader and the melting temperature for peak 1^h (T_1^h) decreased with the increase of the urea concentration in the 0–2 mol l^{-1} urea solution, while the melting temperature of peak 2^h (T_2^h) was found to be independent of the urea concentration in the 0–2 mol l^{-1} urea solution. Similar tendencies are obtained for the aqueous NaCl solution.

The observation of two melting temperatures for the aqueous solution found in this work is interpreted as the phase separation of the homogeneous solution to dense and dilute solutions below 273 K[9,15]. Peak 1^h for the urea and NaCl solutions correspond to the peak for the dilute solution.

D.s.c. heating curves of VI-58 immersed in pure bulk water and in the 2 mol l^{-1} aqueous urea and NaCl solutions are shown in *Figure 6*. Inspecting the Figure, the shape of the d.s.c. heating curves of VI-58 immersed in both urea and NaCl solutions (2 mol l^{-1}) were found to be clearly different to those of the urea and the NaCl solutions and similar to that of VI-58 immersed in pure bulk water. This suggests that the urea and the NaCl solutions in the membranes cannot show the above phenomena found in the aqueous solution. The diffusion of solute and water molecules in the solution should be considered as an important factor in explaining the above phase separation from the homogeneous solution. The diffusion of solute and water in the membranes might be prevented by the polymeric network of the membranes.

The solubilities of urea and NaCl in the freezable bound water of the membranes (S_1) can be estimated from the melting point depression in the membranes immersed in solution (ΔT), the value of melting point depression in water (K_m) and a relationship[16] between concentration and density of the solution. S_1 is defined as C_1/C_0 where C_1 is the solute concentration in the freezing water in the membranes and C_0 is the outer concentration (2.0 mol l^{-1} in this study). The relation between ΔT and molality (m_s) is given as equation (3)[9]

$$\Delta T = K_m m_s \qquad (3)$$

where K_m is reported to be 1.86 K/mol kg^{-1}.[9] Since a degree of melting point depression ($\Delta T = 4$ K) was observed for both peak 1^h and peak 2^h for VI-58 and VI-45

Figure 5 D.s.c. heating curves of pure water (curve A); 2 mol l^{-1} urea (curve B); 2 mol l^{-1} NaCl (curve C) solution, heating rate = 1.25 K/min

Table 3 Melting temperature of water-swollen PVA–IA membranes immersed in aqueous urea solution, heating rate = 1.25 K/min

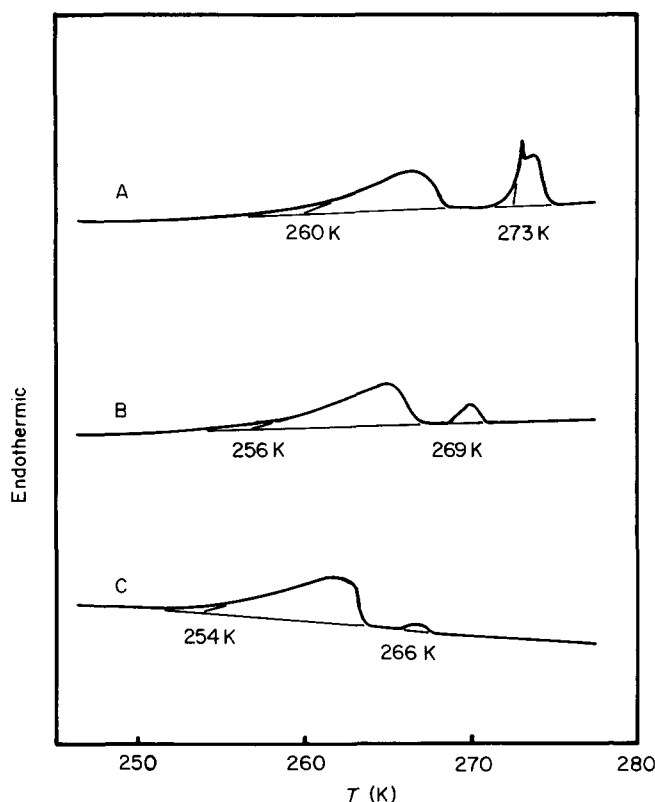| Sample	H	T_1^h	T_2^h	T_1^h	T_2^h	T_1^h	T_2^h	T_1^h	T_2^h
		in water		in 0.02 mol l^{-1}		in 0.2 mol l^{-1}		in 2.0 mol l^{-1}	
				in bulk solution (K)					
Urea solution		273		273		272	262	266	262
				in membranes (K)					
VI-58	0.58	273	260	273	263	273	263	269	256
VI-45	0.45	273	248	273	248	273	248	269	243

Figure 6 D.s.c. heating curves of water-swollen membranes immersed in pure water (curve A); 2 mol l^{-1} urea (curve B); 2 mol l^{-1} NaCl (curve C) solution, heating rate = 1.25 K/min

Table 4 Solubilities of urea and NaCl in total, freezing and non-freezing water of water-swollen PVA–IA membranes. $H = 0.58$, $v_1 = 0.57$, $v_2 = 0.43$

Solute	S	S_1	S_2
Urea	1.1	1.0	1.2
NaCl	0.62	0.94	0.20

solubility of solutes in non-freezing water was found to depend on the solute species. It was observed that S_2 of urea is larger than unity while S_2 for NaCl is found to be less than unity.

The active layer of the membranes, used for desalination, is thought to have only non-freezing water contained within it, and the solubility of NaCl in the water is known to be close to zero[4,19,20]. This is, therefore, consistent with the results obtained in this work. It is concluded that non-freezing water has a selectivity for the solutes such as NaCl and urea and that the property of the freezing water is similar to that of the pure bulk water.

immersed in a 2.0 mol l^{-1} urea solution, S_1 was estimated to be 1.0 for both membranes. S_1 for NaCl in VI-58 was also estimated assuming that NaCl was completely dissociated in the membranes, and tabulated in *Table 4* together with the results for urea.

The solubility of the solutes in the non-freezing water of the membranes (S_2) can also be estimated by equation (4)[17].

$$S = v_1 S_1 + v_2 S_2 \qquad (4)$$

where S is the solubility determined by the desorption method[10,11], v_1 is the volume fraction of freezing water in the total water obtained in *Figure 4* and $v_2 = 1 - v_1$. The values of S, S_1 and S_2 are shown in *Table 4*. S_1 for both NaCl and urea is found to be approximately unity, suggesting that there is no sieving effect[18] for solutes in the freezing water and that the properties of the freezing water are similar to that of pure bulk water. However, the

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