Permeability through cellulose membranes grafted with vinyl monomers in a homogeneous system: 5. 2-Hydroxyethyl methacrylate grafted cellulose membranes

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The homogeneous grafting of 2-hydroxyethyl methacrylate (HEMA) onto cellulose was carried out in a dimethyl sulphoxide (DMSO)–paraformaldehyde solvent system. Three kinds of membranes were prepared: membranes of graft copolymers using ammonium persulphate (APS) as an initiator, membranes of graft copolymers using azobisisobutyronitrile (AIBN), and blended membranes of cellulose and poly(2-hydroxyethyl methacrylate). The diffusive permeabilities of solutes through the membranes, the states of water in them, and their microphase separated structures were investigated. Permeability through the APS and AIBN membranes was better than that through the membrane cast from the DMSO solution of cellulose. The states of water in the membranes were influenced by grafting HEMA onto cellulose. The fine microphase separated structure was essential for the improvement of the permeability through the membranes.

(Keywords: cellulose; 2-hydroxyethyl methacrylate; graft copolymer membrane; diffusive permeability; microphase separated structure; states of water)

INTRODUCTION

Different states of water exist in water-swollen membranes[1-12]. Some water moledules, referred to as 'bound water', are bound to polymer molecules through hydrogen bonding and are thought to be less capable of dissolving solutes[13]. Other water molecules, referred to as 'free water', do not take part in hydrogen bonding. Still other water molecules interacting weakly with polymer molecules are referred to as 'intermediate water'. It has been reported that some solutes can permeate the bound water regions[2,14] and that solutes having hydrophilic groups are closely accessible to polymer molecules[5,8,15,16]. Thus characterization and quantification of water relating to the diffusive permeation of solutes through membranes seem to be significant for clarifying the mechanism of membrane permselectivity.

The difference in affinity of membrane substrates for water results in the different states of water in membranes. The water affinity of copolymers or polymer blends composed of hydrophilic and hydrophobic segments depends on their compositions. In a series of studies[17-20], we have used cellulose with high mechanical strength in water-swollen states as the hydrophilic membrane substrate. Homogeneous grafting of hydrophobic vinyl monomers onto cellulose was carried out in a dimethyl sulphoxide–paraformaldehyde (DMSO–PF) solvent system, yielding copolymers of different compositions. The diffusive permeabilities of solutes through these membranes and the states of water in them were investigated. The grafting of hydrophobic monomers onto hydrophilic cellulose influenced the states of water in the membranes, especially intermediate water, to improve the permeabilities of solutes. Moreover, the fine microphase separated structures were essential for the change in the states of water in the membranes.

It is known that 2-hydroxyethyl methacrylate (HEMA) is an amphiphilic monomer because of its α-methyl and hydroxy groups[21]. Thus it is expected that the states of water in HEMA grafted cellulose membranes differ from those in hydrophobic monomer grafted membranes. In this paper, the permeabilities of solutes through HEMA grafted membranes of various compositions are investigated in relation to the composition, microphase separated structures, and states of water in them.

EXPERIMENTAL

Grafting and membrane preparation

Homogeneous grafting of HEMA onto cellulose in the DMSO–PF solvent system and characterization of the products were performed by the method described in previous papers[22-24].

The homogeneous symmetrical membranes were prepared by the same method as that described previously[17]. The crude reaction mixtures were cast at room temperature on glass plates, and DMSO and

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unreacted HEMA were allowed to evaporate at about 40°C under reduced pressure for 24 h before the coagulation of membranes in water. The HEMA grafted membranes contain the homopolymer component because it is not extracted. The DMSO solutions of cellulose and poly(2-hydroxyethyl methacrylate) (PHEMA) were mixed to give proper blend ratios. The blended membranes were also prepared by the method described above.

Diffusive permeability

The permeabilities of solutes, P, were measured at given temperatures from 20.0 to 50.0°C by the method described in a previous paper[17]. Nine solutes of different molecular weight were used. The viscosity average molecular weights, M_v, for three commercial poly(ethylene glycol) (PEG) samples were estimated from the intrinsic viscosities, $[\eta]$, obtained with benzene at 25.0°C[25]: PEG-IV = 3.1×10^3, PEG-VI = 8.0×10^3 and PEG-XX = 3.1×10^4.

Hydraulic permeability

The hydraulic permeability of water was measured at 30.0°C with a reverse osmosis batch cell (Fuji Seiki FMD300) having a volume of 300 cm^3 and an effective membrane area of 24.6 cm^2 (ref. 17).

Transmission electron microscopy (TEM)

A Hitachi HU-11A transmission electron microscope was used to observe the microphase separated structures of the membranes[17]. The membranes were stained with osmic acid vapour for 24 h. The copolymer of n-butyl methacrylate and methyl methacrylate was used as an embedding medium. The embedded membranes were cross-sectioned at a thickness of approximately 50 nm.

Differential scanning calorimetry (d.s.c.)

The measurements were performed with SEIKO SSC/560 d.s.c. according to the method described previously[18]. The water-swollen membranes were cooled with liquid nitrogen at a rate of 5°C min^{-1} to −80°C and then heated at the same rate to 60–90°C. The weight of each sample was ≈10–20 mg. The water content was varied by standing the sample pan in the d.s.c. cell at a given temperature for a given period to evaporate water. The water content was expressed as the ratio of the weight of water in the membrane to that of the dry membrane.

RESULTS AND DISCUSSION

Copolymers indicate various microphase separated structures according to their compositions and architectures[26]. As mentioned above, the HEMA grafted membranes contain the homopolymer component. Thus the microphase separated structures of the membranes depend not only on the total PHEMA content but also on the grafting efficiency (*GE*), i.e. the ratio of weight of graft polymer to that of polymer formed. Three kinds of membranes are characterized in *Table 1*. The HEMA grafted membranes were classified into two groups according to the initiators used, i.e. ammonium persulphate (APS) and azobisisobutyronitrile (AIBN). It is known that a difference in initiator influences grafting efficiency[28], and that the use of AIBN results in less efficient grafting because of the resonance stabilization of its radical fragments[22–24,28,29]. The difference in grafting efficiency for the three kinds of membranes is obvious. The number of grafts for the AIBN membranes is small.

Figure 1 shows a TEM micrograph of the g-PHEMA 2 membrane, an APS membrane. The dark domains indicate the cellulose phases stained with osmic acid. The cellulose and PHEMA phases are mixed finely with each other and the interfaces between them are not clear. The TEM micrographs of the AIBN membranes are shown in *Figure 2*. The PHEMA phases of the g-PHEMA 12 membrane shown in *Figure 2(a)* are larger than those of the g-PHEMA 2 membrane and are dispersed in the dark matrix. Note that the microphase separated structures for the g-PHEMA 12 membrane, though not quantitative, are rougher than those for the APS membranes. The microphase separated structures for the g-PHEMA 13 membrane, however, are as fine as those of the APS membranes. The other AIBN membranes also indicated similar fine microphase separated structures. The

Table 1 Characterization of membranes[22–24]

Sample code	*GE* (%)	PHEMA content (%)			$10^{-4} M_v$ for grafts[a]	Number of grafts
		Overall	Graft-PHEMA	Homo-PHEMA		
APS membrane						
g-PHEMA 1	71.8	26.0	18.7	7.3	15	0.27
g-PHEMA 2	66.9	33.9	22.7	11.2	–	–
g-PHEMA 3	72.4	35.6	25.8	9.8	2.5	1.8
g-PHEMA 4	46.1	41.9	19.3	22.6	–	–
g-PHEMA 5	58.2	47.7	27.8	19.9	10	0.85
AIBN membrane						
g-PHEMA 11	32.8	11.0	3.6	7.4	15	0.11
g-PHEMA 12	4.7	17.3	0.8	16.5	11	0.01
g-PHEMA 13	37.5	27.2	10.2	17.0	26	0.09
g-PHEMA 14	36.6	35.6	13.0	22.6	41	0.08
Blended membrane[b]						
b-PHEMA 1	0	10.0	0	10.0		
b-PHEMA 2	0	20.0	0	20.0		
b-PHEMA 3	0	30.0	0	30.0		
b-PHEMA 4	0	40.0	0	40.0		

[a] Estimated from $[\eta]$ obtained in dimethyl formamide at 25.0°C[27]
[b] The values of M_v for cellulose and PHEMA are 16×10^4 and 22×10^4, respectively

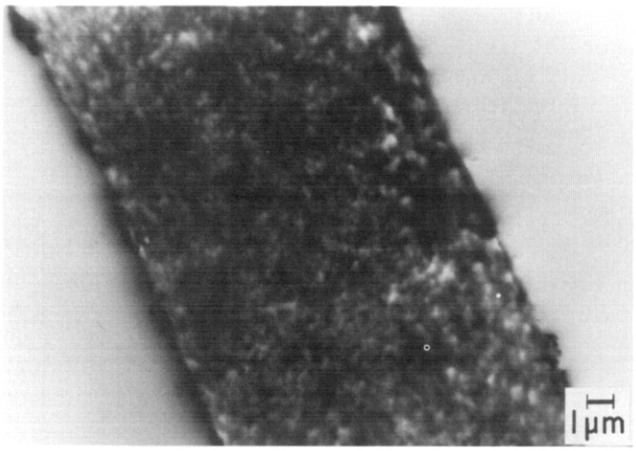

Figure 1 TEM micrograph of the g-PHEMA 2 membrane, an APS membrane, stained with osmic acid

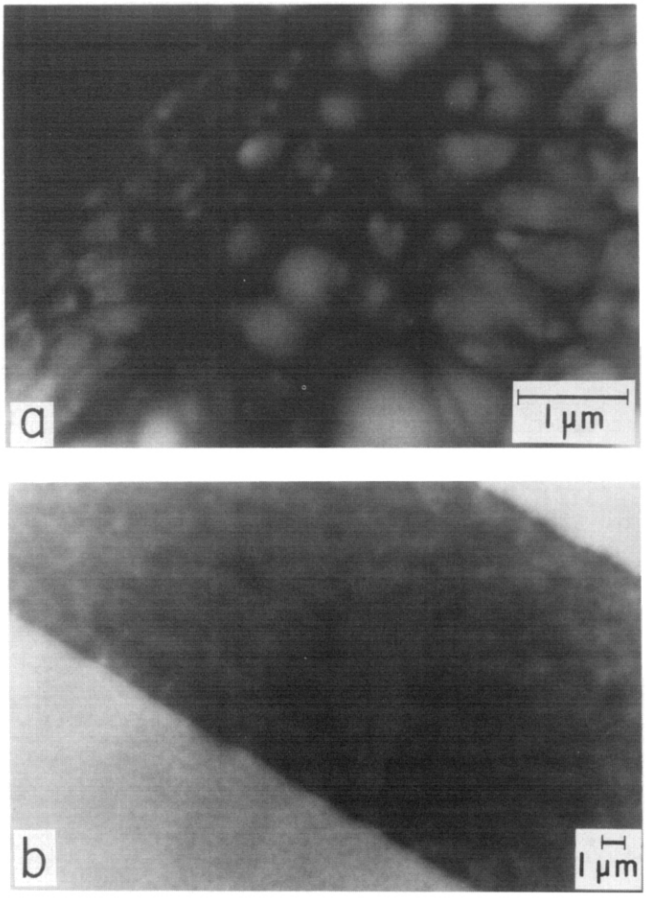

Figure 2 TEM micrographs of the following AIBN membranes: (a) g-PHEMA 12; (b) g-PHEMA 13

microphase separated structures for the hydrophobic monomer grafted cellulose membranes depended on the kind of initiators[17,19,20]. But this is not the case for the HEMA grafted membranes, except for the g-PHEMA 12 membrane indicating the lowest grafting efficiency. This will be because of the good compatibility of cellulose with PHEMA.

Figure 3 shows a TEM micrograph of the b-PHEMA 4 membrane, a blended membrane. The PHEMA phases are dispersed as grey stripes. The microphase separated structures for the blended membrane differ from those for the grafted ones. In our previous papers[17,19,20], the microphase separated structures for the membranes depended on the kind of membranes. But the improvement of permeability through the membranes was recognized only for the APS membranes indicating fine microphase separated structures. Therefore, it would be better to keep in mind that the grafted membranes, except for the g-PHEMA 12 membrane, indicated fine microphase separated structures.

Figure 4 demonstrates the solute molecular weight dependence of permeability for various kinds of membranes. The results of our previous study[17] for the commercial regenerated cellulose membrane, Cuprophan, and the membrane cast from the DMSO solution of cellulose, designated as the cellulose membrane, are also indicated. The permeability through each membrane decreases with increasing molecular weight of the permeant. There is almost no difference in permeabilities through the g-PHEMA 2 membrane, an APS membrane, and g-PHEMA 13 membrane, an AIBN membrane. The permeabilities of lower molecular weight solutes through both membranes are slightly better than those through the Cuprophan membrane, whereas those of three PEG samples are inferior to those through the Cuprophan membrane. A similar peculiarity of permeation for PEG

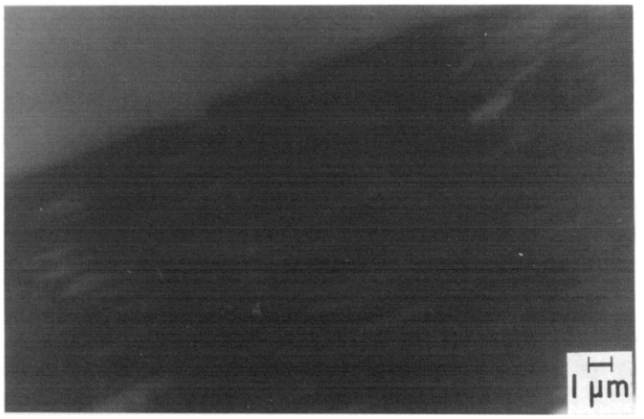

Figure 3 TEM micrograph of b-PHEMA 4 membrane, a blended membrane

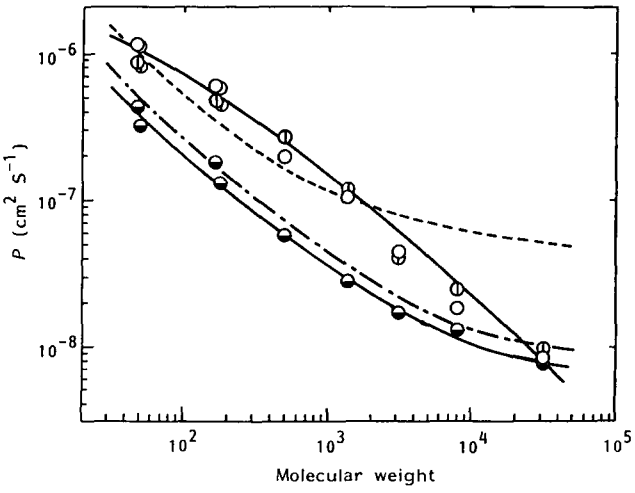

Figure 4 Solute molecular weight dependence of diffusive permeability at 30°C for various kinds of membranes: ○, g-PHEMA 2 membrane; ◑, g-PHEMA 13 membrane; ◒, b-PHEMA 3 membrane; – – –, Cuprophan membrane; –·–·–, cellulose membrane. The solutes are, in the order of increasing molecular weight: NaCl, urea, uric acid, glucose, raffinose, vitamin B_{12}, PEG-IV, PEG-VI and PEG-XX

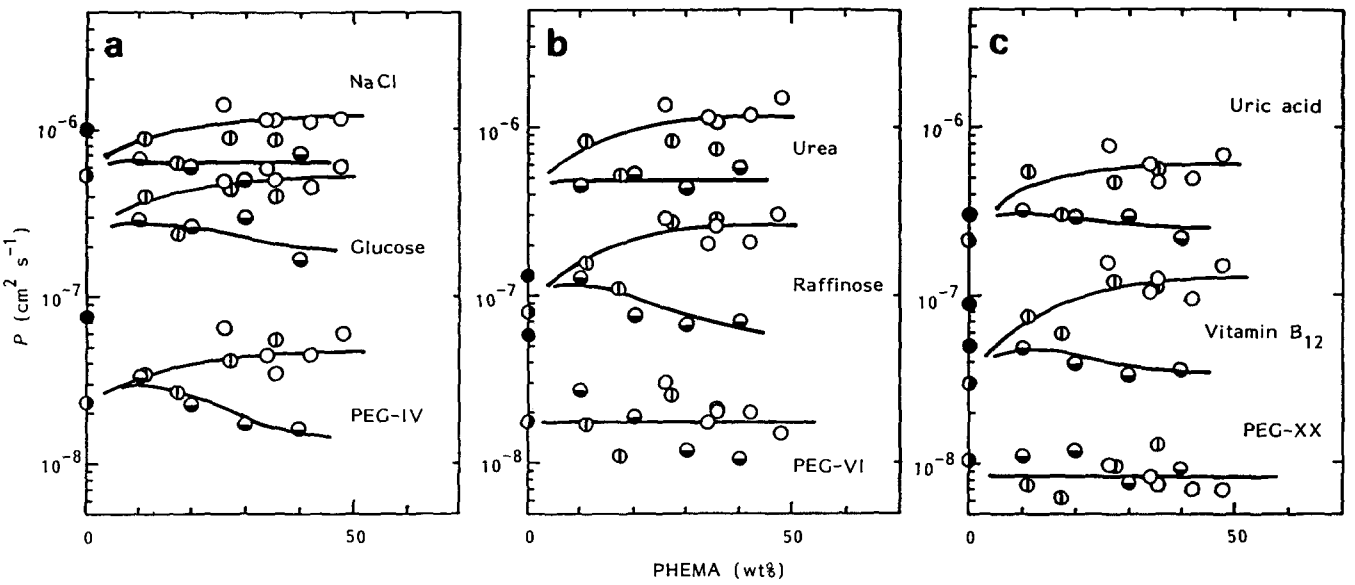

Figure 5 PHEMA content dependence of diffusive permeability for various solutes: ○, APS membranes; ◐, AIBN membranes; ◒, blended membranes; ●, Cuprophan membrane; ◑, cellulose membrane

has been obseved for the hydrophobic monomer grafted membranes[17,19,20]. On the other hand, the solute molecular weight dependence of permeability for b-PHEMA 3, a blended membrane, is similar to that for the cellulosic membranes. In *Table 1*, the PHEMA content for these three kinds of membranes is about 30%, but the grafting efficiencies differ. The solute molecular weight dependence of permeability for the g-PHEMA 12 membrane was also similar to that for the cellulosic membranes.

Figure 5 reveals the relationship between PHEMA content and permeability for various solutes. The data for the cellulosic membranes are also indicated[17]. The permeabilities of solutes through the APS and AIBN membranes, except for the g-PHEMA 12 membrane, are almost on the same level, and increase slightly with increasing PHEMA content and level off. On the other hand, the permeabilities through the blended and g-PHEMA 12 membranes depend little on the PHEMA content or decrease with increasing PHEMA content. The permeabilities of two PEG samples seem independent of the kind of membranes because of their low permeabilities through the APS and AIBN membranes. As can be seen from the TEM micrographs, the microphase separated structures of the g-PHEMA 12 and blended membranes differed from those of the other HEMA grafted membranes. It is clear that the permeability through the membranes depends on the microphase separated structures.

Apparent activation energies for permeation of solutes and hydraulic permeation of water through the water-swollen membranes are listed in *Table 2*. The data of our previous study[20] for the cellulosic membranes are also indicated. Activation energies through the three kinds of membranes are very similar to those through the cellulosic membranes. However, the difference in activation energy is recognized for PEG-VI. Activation energies through the HEMA grafted membranes, except for the g-PHEMA 12 membrane, are larger than those through cellulosic and blended membranes. This is consistent with the lower permeability of PEG through the HEMA grafted membranes than through the cellulosic membranes, indicating the difference in the permeation mechanism for PEG or the specific

Table 2 Apparent activation energy for permeation of solutes and hydraulic permeation of water

	Apparent activation energy (kcal mol^{-1})						
Sample code	NaCl	Urea	Uric acid	Raffinose	Vitamin B_2	PEG-VI	Water
Cellulosic membrane							
Cuprophan	4.8	3.8	4.6	4.6	4.4	3.2	4.2
Cellulose	4.2	4.3	4.8	5.1	5.0	3.2	3.6
APS membrane							
g-PHEMA 2	3.9	4.2	4.5	5.0	4.9	5.5	3.9
g-PHEMA 4	4.7	4.3	4.4	4.5	4.4	4.6	3.5
AIBN membrane							
g-PHEMA 11	4.5	4.1	4.8	4.9	5.0	4.7	–
g-PHEMA 12	4.7	4.3	5.3	5.3	5.2	3.4	4.1
g-PHEMA 14	4.2	4.5	5.1	5.1	4.1	4.4	–
Blended membrane							
b-PHEMA 1	4.7	4.6	4.5	4.8	4.5	3.3	–
b-PHEMA 3	4.3	4.8	4.5	4.5	4.5	3.5	4.1

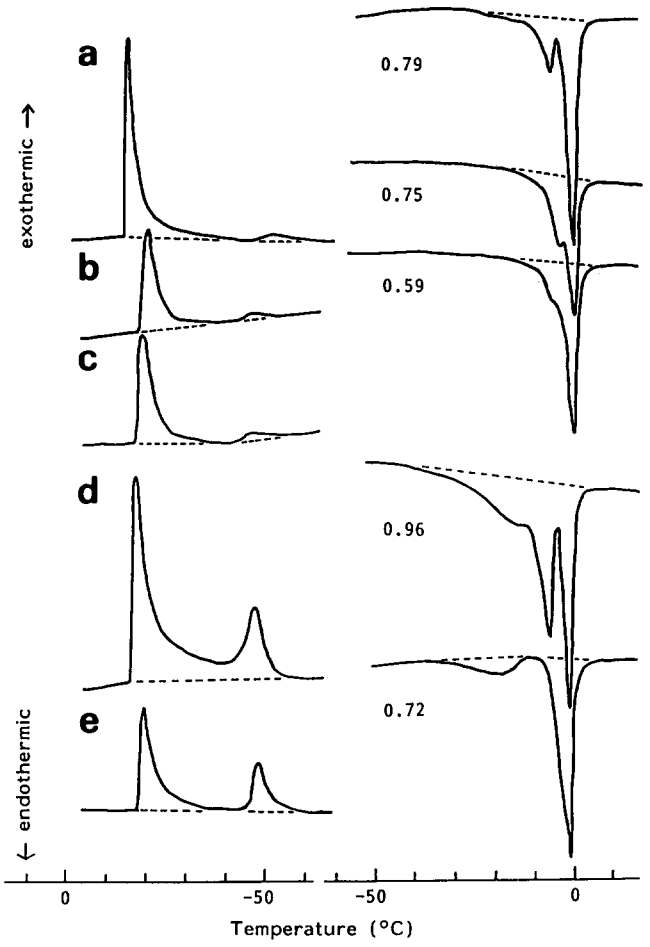

Figure 6 D.s.c. freezing and melting thermograms for various kinds of membranes: (a) g-PHEMA 1; (b) g-PHEMA 14; (c) b-PHEMA 3; (d) Cuprophan; (e) cellulose. Numbers on curves give water content

interaction between the HEMA grafted membranes and PEG. It is of interest that the difference in activation energy is recognized only for PEG. The difference in activation energy for PEG has been also reported for methyl methacrylate grafted membranes[20].

Freezing and melting thermograms for various kinds of water-swollen membranes are drawn in *Figure 6*. Many peaks are found on both sets of thermograms, indicating the presence of several states of freezing water. Both the sharp exothermic peak at around −20°C and the sharp endothermic peak at around 0°C are assigned to free water[18]. The other peaks at lower temperatures are assigned to intermediate water[18]. The non-freezing water, which does not freeze even when cooled down far below the freezing point, is regarded as bound water[30]. As can be seen from the melting thermogram for the Cuprophan membrane, even in intermediate water, there exists water differing in its interaction with polymer molecules, i.e. relatively weakly interacting water at higher temperatures and relatively strongly interacting water at lower temperatures[2,4]. The thermograms for the HEMA grafted and blended membranes are different from those for the cellulose membrane. The exothermic peaks at around −50°C become small. The endothermic peaks at around −20°C almost disappear but the peaks re-appear at around −5°C. The endothermic peak at around −20°C decreased with increasing PHEMA content. The endothermic peak at around −5°C for the b-PHEMA 3 membrane is not as remarkable as those for the HEMA grafted membranes. A comparison of these thermograms reveals that the incorporation of amphiphilic PHEMA into hydrophilic cellulose influences the states of water in the membranes, especially the states of intermediate water, and that the degree of influence depends on their microphase separated structures. A similar influence on the states of intermediate water was also observed for hydrophobic monomer grafted membranes, but the degree of influence differed from one to another[18–20]. Both thermograms for the hydrophobic polymer blended cellulose membranes were similar to those for the cellulose membrane. But this is not the case for the PHEMA blended ones. This may be because of the amphiphilicity of PHEMA.

The water content was varied to investigate its influence on the states of water in the membranes. On both thermograms, the free water peaks decreased more sharply than the intermediate water peaks with decreasing water content, but the relatively strongly interacting water peaks hardly decreased. A shift of peak temperature was also observed, as depicted in *Figure 7*. The free water peak temperatures shift toward lower temperatures with decreasing water content. In particular, the exothermic free water peak temperature changes sharply at around 0.8 water content. On the other hand, the peak temperatures for intermediate water scarcely shift. These results indicate that the water molecules interacting more weakly with polymer molecules decrease faster than those interacting more strongly with decreasing water content[2,6,10,11,18–20].

Figure 8 illustrates the relationship between the water content and heat of fusion of freezing water, ΔH, determined from the area under the endothermic curve. The data points for each membrane do not follow a straight line but give a curve convexing downward at lower water contents. The slope of the straight part of each curve is equal to the specific heat of fusion of pure water. This indicates that the amount of non-freezing

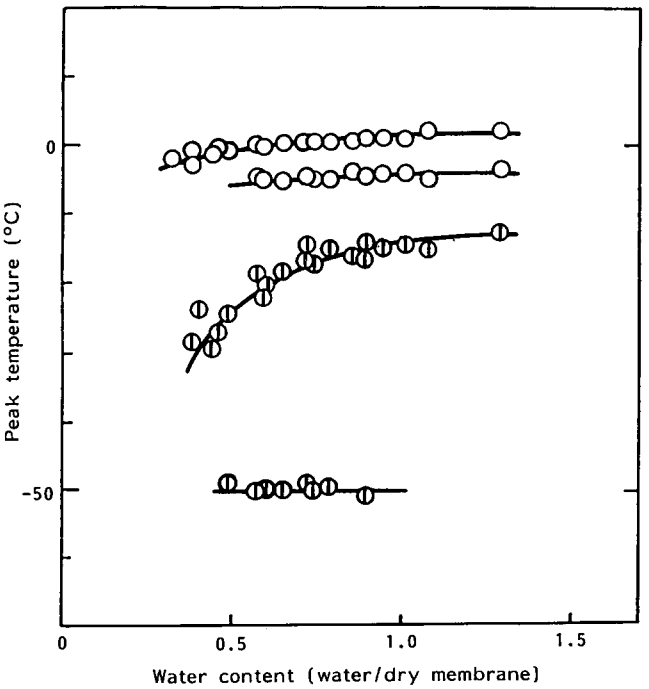

Figure 7 Effects of water content on the endothermic peak (○) and exothermic (◑) peak temperatures for g-PHEMA 1

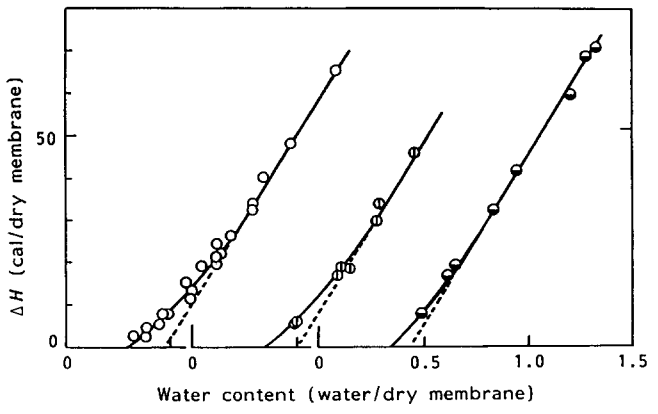

Figure 8 Total water content dependence of the heat of melting of freezing water for various kinds of membranes: ○, g-PHEMA 1; ◑, g-PHEMA 11; ◒, b-PHEMA 1

water is not saturated at lower water contents since, except for some cases[12,31,32], it is assumed that the specific heat of fusion of freezing water is equal to that of pure water. Such results have also been reported for other membranes[2,3,18–20].

The equilibrium non-freezing water content, W_{non}, was estimated by extrapolation of the straight part of the curve to $\Delta H = 0$. The results are summarized in *Table 3*. As mentioned in our previous paper[18], the equilibrium water content determined by blotting water on the membrane surfaces, W_{blot}, involved a considerable experimental error. It has been indicated[18–20] that there exists good correlation among W_{blot}, the water content where the peak temperature for exothermic free water changes sharply in *Figure 7*, and the water content where the curve deviates from a straight line in *Figure 8*. Thus, in this study, their average value was also used as the equilibrium water content estimated by the d.s.c. method, $W_{d.s.c.}$. The results are listed in *Table 3*. The amount of equilibrium freezing water thought to be related to the permeation of solutes was taken as the difference between $W_{d.s.c.}$ and W_{non}.

The values of $W_{d.s.c.}$ and W_{non} for the HEMA grafted membranes are larger than those for the cellulose membrane. Such a result was not obtained for the hydrophobic monomer grafted membranes[18–20], indicating the influence of amphiphilic PHEMA. Moreover, the freezing water contents for the HEMA grafted membranes, except for the g-PHEMA 12 membrane, are larger than that for the cellulose membrane. This result is consistent with those shown in *Figures 4* and *5*. The freezing water contents for the blended membranes are almost the same as that for the cellulose membrane. On the other hand, the freezing water content for the Cuprophan membrane is the largest, being inconsistent with the results shown in *Figures 4* and *5*. It is difficult to elucidate the better permeability through the HEMA grafted membranes by means of differences in freezing water content, suggesting that the freezing water content is not the only measure of solute permeability. The endothermic curves shown in *Figure 6* can be resolved roughly into each state of water. The results are also summarized in *Table 3*. The amount of free water for the Cuprophan membrane is comparable to those for the APS membranes but not to those for the AIBN membranes. In spite of comparable permeabilities through the APS and AIBN membranes, the amounts of free water for the two kinds of membranes differ from each other. The amounts of free water and relatively weakly interacting intermediate water may be a main parameter for solute permeation. The quantification of each state of water will be necessary in order to discuss the membrane permselectivity in relation to the states of water in membranes. Moreover, partition of solute among different states of water, interaction between solute and membrane substrate, and so on, must be taken into account. The quantification of these parameters, however, is not sufficient at the present stage.

Table 3 Amounts of water in membranes

Sample code	Equilibrium water content[a], $W_{d.s.c.}$	Equilibrium non-freezing water content[a], W_{non}	Equilibrium freezing water content[a]			
			Overall	Free water	Intermediate water	
					Weakly interacting	Strongly interacting
Cellulosic membrane						
Cuprophan	1.00	0.49	0.51	0.24	0.14	0.13
Cellulose	0.70	0.45	0.25	0.22	–	0.03
APS membrane						
g-PHEMA 1	0.80	0.47	0.33	0.24	0.08	0.01
g-PHEMA 2	0.77	0.46	0.31	0.22	0.08	0.01
g-PHEMA 4	0.78	0.50	0.28	0.24	0.04	–
g-PHEMA 5	0.75	0.45	0.30	0.23	0.07	–
AIBN membrane						
g-PHEMA 11	0.75	0.50	0.25	0.19	0.05	0.01
g-PHEMA 12	0.70	0.46	0.24	0.14	0.08	0.02
g-PHEMA 13	0.72	0.45	0.27	0.18	0.08	0.01
g-PHEMA 14	0.75	0.45	0.30	0.17	0.13	–
Blended membrane						
b-PHEMA 1	0.69	0.43	0.26	0.19	0.06	0.01
b-PHEMA 2	0.65	0.40	0.25	0.20	0.04	0.01
b-PHEMA 3	0.63	0.40	0.23	0.20	0.03	–
b-PHEMA 4	0.62	0.40	0.22	0.19	0.03	–

[a] Weight of water in membrane/weight of dry membrane

CONCLUSIONS

The diffusive permeabilities of various solutes through HEMA grafted cellulose membranes and the states of water in them were investigated. The incorporation of amphiphilic PHEMA into cellulose influenced the states of intermediate water in the membranes. An improvement in permeability through the membranes was observed for the membranes with fine microphase separated structures.

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