Permeability through Cellulose Membranes Grafted with Vinyl Monomers in a Homogeneous System. VII. Acrylamide Grafted Cellulose Membranes

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Synopsis

The homogeneous grafting of acrylamide (AAm) onto cellulose was carried out in a dimethyl sulfoxide/paraformaldehyde (DMSO/PF) solvent system. The diffusive permeabilities of solutes through the AAm-grafted cellulose membranes, apparent activation energy for solute permeation through them, states of water in them, and their microphase separated structures were investigated. The permeability through the grafted membranes was superior to that through the cellulose membrane cast from the DMSO/PF solution of cellulose. The total water contents of the grafted membranes were larger than that of the cellulose membrane. The state of intermediate water in the grafted membranes with fine microphase separated structures was influenced remarkably. A higher activation energy was observed for the solutes with poor permeability through the membranes.

INTRODUCTION

It is known that different states of water are present in water-swollen membranes.[1-15] The amount of each state of water in membranes varies with the affinity of membrane substrates for water. In a series of studies,[16-21] we have investigated the relationship between the diffusive permeabilities of solutes through membranes and the amount of each state of water in them to clarify the mechanism of membrane permselectivity. Cellulose grafted with vinyl monomers in a homogeneous solution system has been used as membrane materials. The kind of monomers and composition of copolymers were varied to prepare the membranes of different affinity for water. The change in the states of water in the grafted membranes brought about changes in the permeabilities of solutes through them.

In this paper, we chose a hydrophilic vinyl monomer, acrylamide (AAm). It is expected that the affinity of the membranes for water would increase. The permeabilities of solutes through the AAm-grafted cellulose membranes are investigated in relation to the composition of copolymers, microphase separated structures of the membranes, and states of water in them.

EXPERIMENTAL

Grafting and Membrane Preparation

The homogeneous grafting of AAm onto cellulose in a dimethyl sulfoxide/paraformaldehyde (DMSO/PF) solvent system and the characterization of

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the graft products were performed by the method described in our previous papers.[22-25] The viscosity-average molecular weight M_v of grafted polyacrylamide (PAAm) was estimated from the intrinsic viscosity $[\eta]$ obtained with water at 30.0°C.[26]

The crude grafted mixtures were cast at room temperature on glass plates and dried at about 60°C under reduced pressure for 24 h. After being immersed in water for several days, the membranes were easily peeled off. All membranes were stored in distilled water until use.[16]

Diffusive Permeability

The diffusive permeability P was measured at temperatures from 20.0 to 50.0°C by the method described in the previous paper.[16] Ten solutes of different molecular weights were used. The values of M_v of commercial poly(ethylene glycol) (PEG) samples were estimated from $[\eta]$ obtained with benzene at 25.0°C.[27] The PEG samples were abbreviated as PEG-IV, PEG-VI, and PEG-XX in the order of increasing molecular weight.

Hydraulic Permeability

The flux of water under an applied pressure of 10 kg cm^{-2} was measured 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.

Transmission Electron Microscopy (TEM)

The microphase separated structures of the membranes were observed with a Hitachi HU-11A transmission electron microscope.[16] The membranes were stained with osmic acid vapor for 1 day. The copolymer of *n*-butyl methacrylate, methyl methacrylate, and AAm was used as an embedding medium. The embedded membranes were cut into ultrathin sections of approximately 50 nm thickness.

Differential Scanning Calorimetry (DSC)

The states of water in the membranes were investigated with a SEIKO SSC/560 DSC.[17] The membranes were immersed in pure water and aqueous solutions of NaCl, raffinose, and PEG-VI for several days, the surface water wiped off with paper, and the membranes placed in aluminum pans. The weight of each sample was about 10–20 mg. The samples were cooled with liquid nitrogen at a rate of 5°C/min to −80°C and then heated at the same rate to 80–90°C. The sample pans were allowed to stand in the DSC cell at a given temperature for a given period to evaporate water. The measurements were repeated a few times to vary the total water content. 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

The membranes are characterized in Table I. Two kinds of radical initiators, i.e., ammonium persulfate (APS) and azobisisobutyronitrile (AIBN), were used to synthesize the graft copolymers of different molecular architectures. The

TABLE I
Characterization of AAm Grafted Cellulose Membranes

Membrane	PAAm content (%)	$M_v \times 10^{-4}$ of grafts[a]	Number of grafts[b]
APS membrane			
g-PAAm 1	5.9	0.9	1.0
g-PAAm 2	18.4	—	—
g-PAAm 3	30.0	1.3	3.7
AIBN membrane			
g-PAAm 11	5.5	—	—
g-PAAm 12	7.0	3.0	0.37
g-PAAm 13	13.8	4.6	0.48

[a] Estimated from $[\eta]$ obtained with water at 30.0°C.[26]
[b] M_v of cellulose is 16×10^4.[16]

AAm-grafted cellulose membranes were classified into two groups: APS membrane and AIBN membrane. It is known[28] that AIBN is not suitable as a grafting initiator because of the resonance stabilization of its radical fragments; grafting efficiency is low, and the number of grafts small. As can be seen from Table I, the numbers of grafts of the APS membranes are larger than those of the AIBN membranes.

The TEM micrographs of the APS and AIBN membranes are shown in Figures 1 and 2, respectively. The dark domains indicate the cellulose phases stained with osmic acid. The interfaces between cellulose and PAAm phases of the APS membranes are not clear. White PAAm domains are dispersed finely in the *g*-PAAm 12 membrane, an AIBN membrane. The microphase separated structures of the APS membranes are found to be finer, though not quantitatively, than those of the AIBN membranes. The APS membranes of other vinyl monomer grafted cellulose membranes also indicated similar fine microphase separated structures.[16,18–20]

Figure 3 demonstrates the solute molecular weight dependence of permeability for various kinds of membranes. The results for the commercial regenerated cellulose membrane, cuprophan, and the membrane cast from the DMSO/PF solution of cellulose, named as the cellulose membrane, are also indicated.[16] The permeability through the *g*-PAAm 2 membrane, an APS membrane, is superior to that through the cellulose membrane. The permeabilities of intermediate molecular weight solutes, i.e., uric acid, glucose, and raffinose, are superior to those through the cuprophan membrane. The permeability through the *g*-PAAm 13 membrane, an AIBN membrane, is also superior to that through the cellulose membrane, but not as good as that through the cuprophan membrane.

Figure 4 reveals the relationship between the PAAm content and permeability for various solutes. The data for the cellulosic membranes are also included.[16,20] None of the solute permeabilities depend on the PAAm content. The permeabilities of solutes, except for uric acid, glucose, and raffinose, are also independent of the kind of membranes. The permeabilities of uric acid, glucose, and raffinose through the APS membranes are superior to those through the cuprophan membrane. The permeabilities of PEG–XX and hemoglobin through

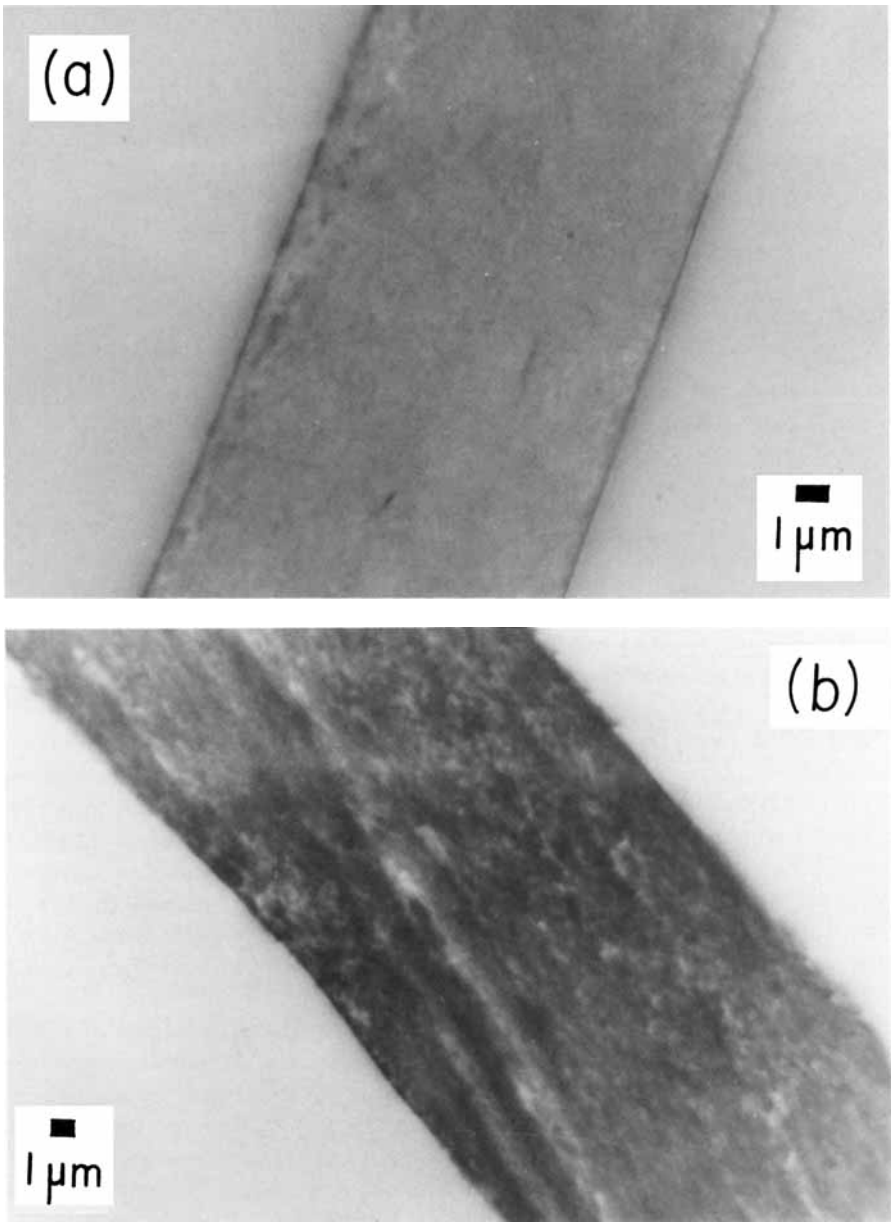

Fig. 1. TEM micrographs of the APS membranes stained with osmic acid: (a) *g*-PAAm 1; (b) *g*-PAAm 3.

the grafted membranes are slightly inferior to those through the cellulose membrane. It is noted that only the permeabilities of intermediate molecular weight solutes reflect the difference in the microphase separated structures of the grafted membranes.

Freezing and melting thermograms of the membranes swollen in water are drawn in Figure 5. The result for the cellulose membrane is also drawn.[17] Many peaks are found on both thermograms, indicating the presence of several states

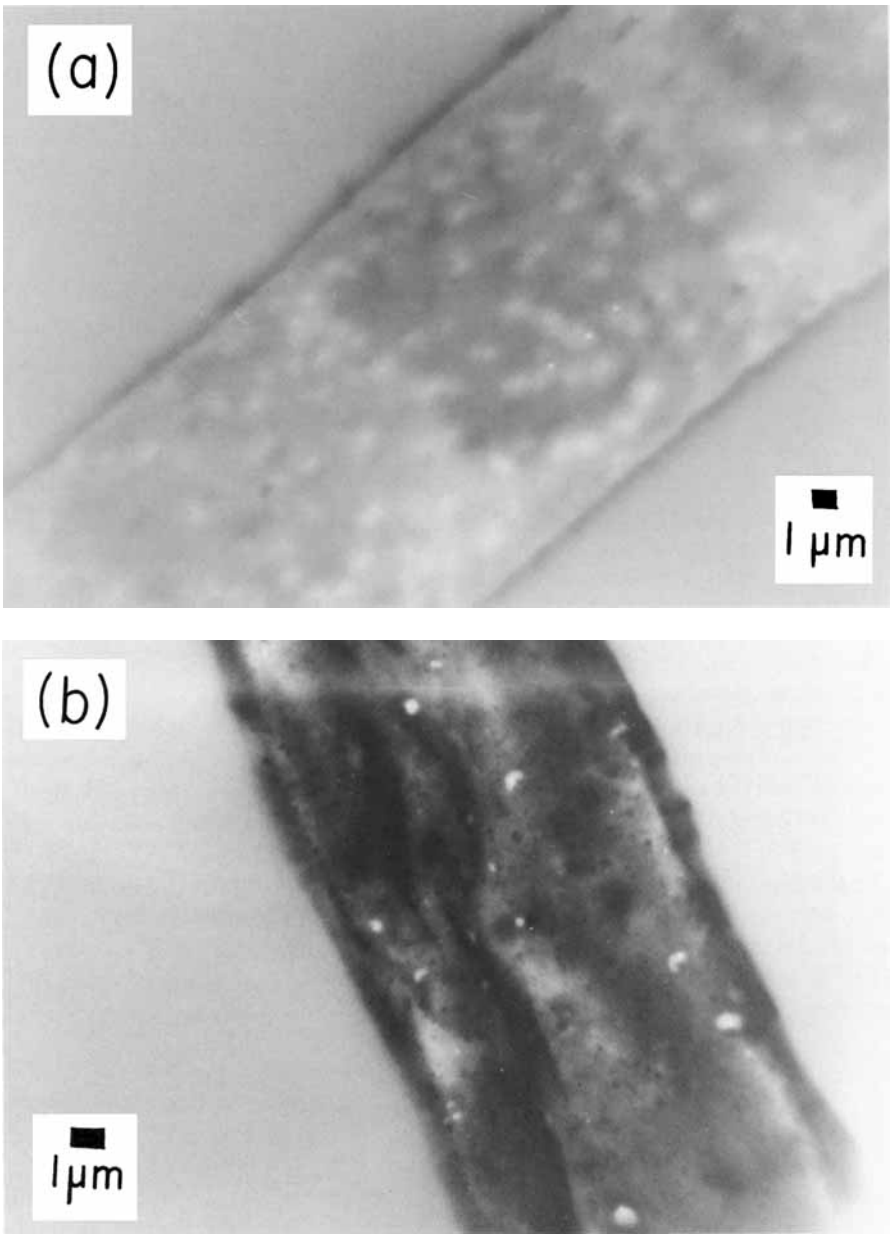

Fig. 2. TEM micrographs of the AIBN membranes: (a) *g*-PAAm 12; (b) *g*-PAAm 13.

of freezing water. The exothermic peak at around −20°C and the endothermic peak at around 0°C are assigned to free water. The other peak at lower temperatures is assigned to intermediate water interacting weakly with polymer molecules. The nonfreezing water, which does not freeze even when cooled far below the freezing point, is regarded as bound water. The intermediate water peak disappears on both thermograms of the *g*-PAAm 1 membrane. On the other hand, the thermograms of the *g*-PAAm 11 membrane resemble those of

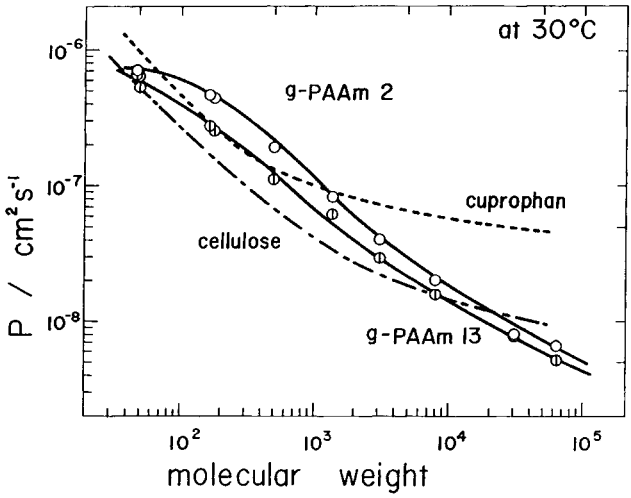

Fig. 3. Solute molecular weight dependence of diffusive permeability at 30°C for various kinds of membranes: (○) *g*-PAAm 2 membrane; (⊕) *g*-PAAm 13 membrane; (– – –) cuprophan membrane; (-·—·—·-) cellulose membrane. The solutes are, in the order of increasing molecular weight, NaCl, urea, uric acid, glucose, raffinose, vitamin B_{12}, PEG-IV, PEG-VI, PEG-XX, and hemoglobin.

the cellulose membrane. The change in the states of water in the membranes was recognized only for the APS membranes with fine microphase separated structures. The presence of the PAAm chains around the cellulose chains appears essential to influence the states of water in the membranes. A similar result has been also recognized for other vinyl monomer grafted cellulose membranes.[17-21]

In the previous studies,[17-20] the states of water in the membranes swollen in water were investigated. However, the difference in permeability through the membranes was not correlated quantitatively with the amount of each state of water. It has been reported[29-32] that the amounts of total water and bound water vary with the permeating solutes. Furthermore, we have reported[21] that

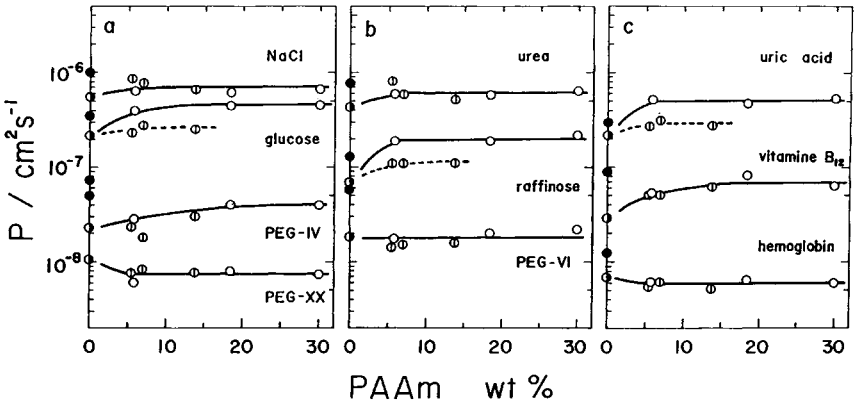

Fig. 4. PAAm content dependence of diffusive permeability at 30°C for various solutes: (○) APS membrane; (⊕) AIBN membrane; (●) cuprophan membrane; (◑) cellulose membrane.

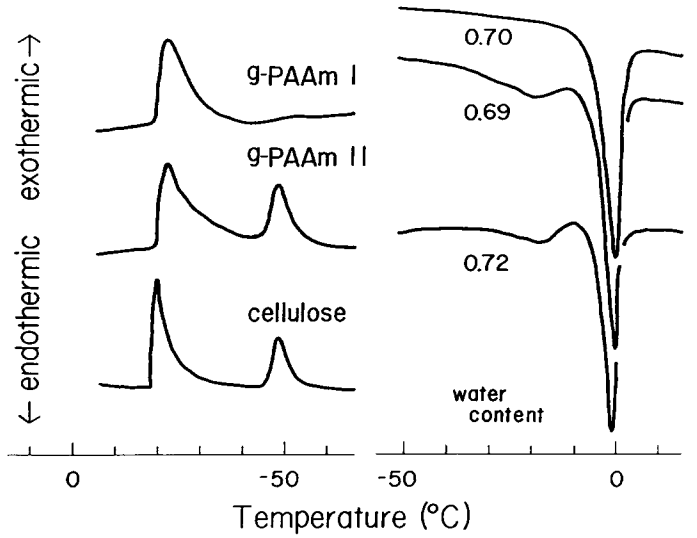

Fig. 5. DSC freezing and melting thermograms of various kinds of membranes swollen in water. Numbers on curves indicate water content.

the amount of free water is influenced by the presence of solutes. The states of water in the membranes swollen in solutions were also investigated in this study.

Figure 6 indicates the freezing and melting thermograms of the *g*-PAAm 12 membranes swollen in pure water and three kinds of aqueous solutions. On the exothermic curves, the free water and intermediate water peaks of the solution-

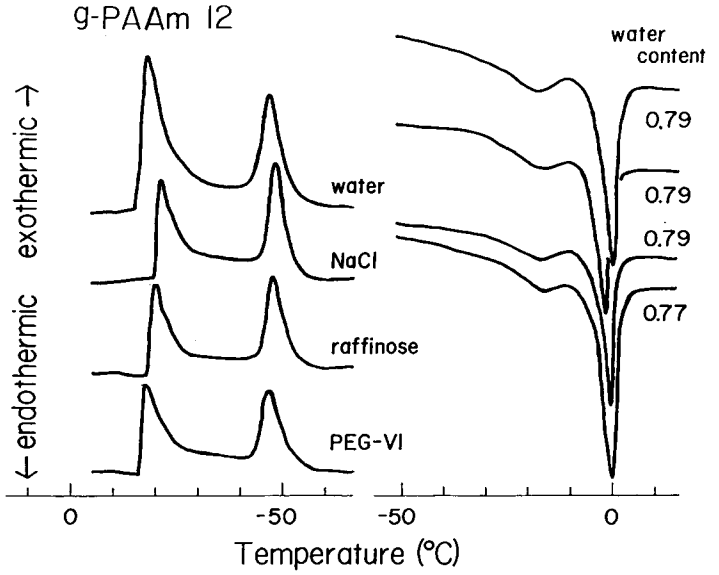

Fig. 6. DSC freezing and melting thermograms of the *g*-PAAm 12 membrane swollen in water and aqueous solutions of NaCl, raffinose, and PEG-VI. Numbers on curves indicate water content.

swollen membranes shift toward lower temperatures. On the endothermic curves, the free water peaks shift toward lower temperatures but the intermediate water peaks shift toward higher temperatures. It has been also reported for other grafted membranes[21] that there is a difference between the direction of peak shift in the freezing process and that in the melting process. The explanation for this is not clear at the present time.

The total water content was varied to investigate its influence on the states of water in the membranes. On both thermograms, with decreasing water content the amount of free water decreased more rapidly than that of intermediate water. As can be seen from Figure 7, the peak temperatures, except for the exothermic intermediate water peak, shift toward lower temperatures with decreasing water content. These results imply that the water molecules interacting more weakly with polymer molecules decrease faster with decreasing water content than those interacting more strongly.[3,8,13,14,17-21]

Figure 8 shows the relationship between the water content and heat of fusion of freezing water, ΔH, determined from the endothermic peak area. The data points for each swollen membrane do not follow a straight line at lower water contents. The slope of the straight part of each curve is equal to the specific heat of fusion of pure water. The amount of freezing water at each water content is calculated from ΔH on the assumption that the specific heat of fusion of freezing water is equal to that of pure water. The amount of nonfreezing water is determined from the difference in the amounts of total water and freezing water. Figure 8 thus reveals that the amount of nonfreezing water decreases at lower water contents. A similar result has also been reported for other membranes.[3,4,17-21] The equilibrium nonfreezing water content W_{non} was estimated by extrapolation of the straight part to $\Delta H = 0$.

As mentioned in the previous papers,[17-21] there existed good correlation among the water content determined by blotting water on the membrane sur-

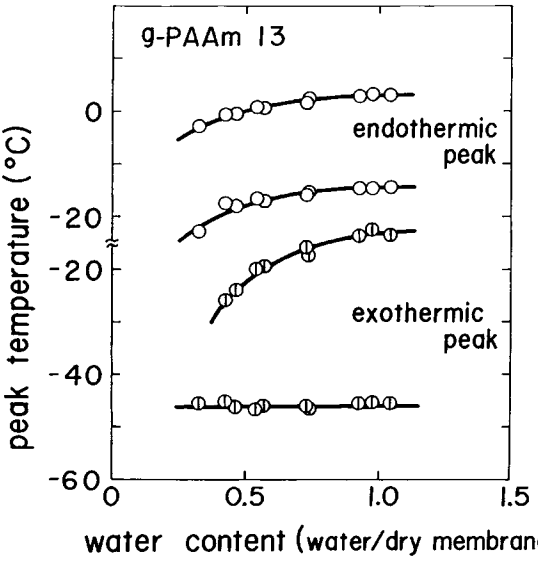

Fig. 7. Effect of water content on the endothermic (○) and exothermic (⊕) peak temperatures of the *g*-PAAm 13 membrane.

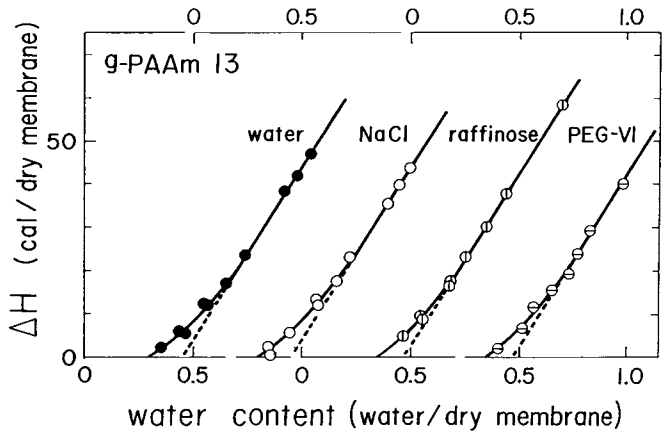

Fig. 8. Total water content dependence of the heat of fusion of freezing water for the *g*-PAAm 13 membrane swollen in water (●) and aqueous solutions of NaCl (○), raffinose (Φ), and PEG-VI (⊖).

faces, the water content where the peak temperature 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 DSC method, W_{DSC}. The equilibrium freezing water content was calculated from the difference between W_{non} and W_{DSC}. The results are summarized in Table II. The data for cellulosic membranes are also listed.[18,21] The values of W_{DSC} of the grafted membranes are larger than that of the cellulose membrane, indicating the influence of hydrophilic PAAm. There is little difference among the membranes swollen in water and three kinds of solutions with regard to W_{DSC} and W_{non}. On the other hand, the endothermic curves shown in Figures 5 and 6 can be resolved roughly into each state of water. The proportions of free water of the solution-swollen cellulosic membranes are less than those of the water-swollen cellulosic membranes. However, the proportions of free water of the solution-swollen AIBN membranes are almost the same as those of the water-swollen AIBN membranes, and depend only slightly on the kind of solutes. These results are comparable with those for other vinyl monomer grafted cellulose membranes, i.e., the difference in the proportion of free water depended on the kind of vinyl monomers.[21]

It has been reported[3,7,11,33-35] that the solute permeable water regions depend on the kind of solutes. If a certain solute can permeate only through the free water regions in membranes, the order of permeability through membranes would correspond to that of free water content of membranes. The amounts of total water and freezing water of the cuprophan membrane are largest of all the membranes tested. The freezing water contents of the APS membranes are at most about 0.3, larger than that of the cellulose membrane, and independent of the PAAm content. The free water contents of the APS membranes are larger than that of the cuprophan membrane. Furthermore, the free water contents of the AIBN membranes are at most about 0.2, but larger than those of the cellulosic membranes. Comparison of Figures 3 and 4 with Table II indicates that the order of permeability of each solute through the membranes does not correspond to that of the amount of any state of water. It is difficult to explain

TABLE II
Amounts of Water in Cellulosic and Grafted Membranes Swollen in Pure Water and Aqueous Solutions of NaCl, Raffinose, and PEG-VI

Membrane	Equilibrium water content W_{DSC}	Equilibrium nonfreezing water content W_{non}	Equilibrium freezing water content		
			Overall	Free water	Intermediate water
	(wt of water in membrane/wt of dry membrane)				
Cuprophan					
Water	1.00	0.49	0.51	0.24 (47%)	0.27 (53%)
NaCl	1.00	0.47	0.53	0.19 (35%)	0.34 (65%)
Raffinose	0.98	0.48	0.50	0.17 (35%)	0.33 (65%)
PEG-VI	0.99	0.47	0.52	0.20 (38%)	0.32 (62%)
Cellulose					
Water	0.70	0.45	0.25	0.22 (88%)	0.03 (12%)
NaCl	0.68	0.44	0.24	0.18 (77%)	0.06 (23%)
Raffinose	0.69	0.44	0.25	0.18 (72%)	0.07 (28%)
PEG-VI	0.68	0.43	0.25	0.19 (74%)	0.06 (26%)
APS membrane					
g-PAAm 1					
Water	0.70	0.43	0.27	0.27	—
NaCl	0.70	0.43	0.27	0.27	—
Raffinose	0.69	0.40	0.29	0.29	—
PEG-VI	0.70	0.41	0.29	0.29	—
g-PAAm 2					
Water	0.75	0.46	0.29	0.29	—
NaCl	0.75	0.47	0.28	0.28	—
Raffinose	0.75	0.47	0.28	0.28	—
PEG-VI	0.75	0.46	0.29	0.29	—
g-PAAm 3					
Water	0.75	0.45	0.30	0.30	—
NaCl	0.75	0.45	0.30	0.30	—
Raffinose	0.75	0.46	0.29	0.29	—
PEG-VI	0.75	0.46	0.29	0.29	—
AIBN membrane					
g-PAAm 11					
Water	0.73	0.49	0.24	0.22 (90%)	0.02 (10%)
NaCl	0.72	0.50	0.22	0.20 (91%)	0.02 (9%)
Raffinose	0.73	0.51	0.22	0.19 (86%)	0.03 (14%)
PEG-VI	0.72	0.50	0.22	0.19 (86%)	0.03 (14%)
g-PAAm 12					
Water	0.80	0.52	0.28	0.20 (72%)	0.08 (28%)
NaCl	0.80	0.53	0.27	0.20 (75%)	0.07 (25%)
Raffinose	0.80	0.54	0.26	0.19 (73%)	0.07 (27%)
PEG-VI	0.80	0.52	0.28	0.22 (78%)	0.06 (22%)
g-PAAm 13					
Water	0.71	0.45	0.26	0.24 (91%)	0.02 (9%)
NaCl	0.70	0.45	0.25	0.23 (92%)	0.02 (8%)
Raffinose	0.70	0.47	0.23	0.21 (90%)	0.02 (10%)
PEG-VI	0.70	0.47	0.23	0.22 (95%)	0.01 (5%)

the difference in the molecular weight dependence of permeability through the membranes in relation to the amount of each state of water.

Apparent activation energies for permeation of solutes and hydraulic permeation of water through the water-swollen membranes are listed in Table III.

TABLE III
Apparent Activation Energy for Permeation of Solutes and Hydraulic Permeation of Water

	Activation energy (kcal mol^{-1})								
Membrane	NaCl	Urea	Uric acid	Glucose	Raffinose	Vitamin B_{12}	PEG-VI	Hemoglobin	Water
Cellulosics									
Cuprophan	4.3	3.8	4.6	4.6	4.6	4.4	3.2	5.3	4.2
Cellulose	4.2	4.3	4.8	4.9	5.1	5.0	3.2	5.6	3.6
APS membrane									
g-PAAm 1	4.4	4.4	4.7	4.3	4.4	4.9	4.5	5.6	3.8
g-PAAm 2	4.5	4.5	4.5	4.5	4.9	4.7	4.1	5.7	3.7
g-PAAm 3	4.6	4.4	4.7	4.7	4.7	4.7	4.4	5.3	3.7
AIBN membrane									
g-PAAm 11	4.7	4.7	4.8	4.2	4.5	4.8	3.5	5.8	3.8
g-PAAm 12	4.4	4.4	4.9	4.7	4.6	5.1	3.5	5.2	3.7
g-PAAm 13	4.8	4.6	4.9	4.6	4.8	4.5	3.8	5.6	3.3

The data for the cellulosic membranes are also shown for comparison.[19,21] The activation energy is thought to be a measure indicating the extent of an interaction between solute and membrane substrate. It has been reported[19-21] that the solutes difficult to permeate through the grafted cellulose membranes show higher activation energies. Activation energies for permeation of NaCl and urea through the grafted membranes are a little larger than those through the cellulosic membranes. Moreover, activation energies for PEG-VI through the APS membranes are larger than those through the cellulosic membranes. This is consistent with the result shown in Figure 3 that the permeabilities of lower and higher molecular weight solutes through the grafted membranes are inferior to those through the cellulosic membranes.

Activation energies for hydraulic permeation of water through the membranes are similar to that for purely viscous flow of water through a rigid capillary.[36] The difference in the amount of each state of water hardly influences activation energy for water through the membranes. A similar result has been reported for other vinyl monomer grafted cellulose membranes.[19-21]

In conclusion, we used hydrophilic AAm as a vinyl monomer. The permeability through the AAm grafted cellulose membranes was superior to that through the cellulose membrane. The permeabilities of intermediate molecular weight solutes through the APS membranes were superior to those through a cuprophan membrane. The total water contents of the grafted membranes were larger than that of the cellulose membrane. The nonfreezing water contents of the grafted membranes also increased. There was little difference between the solution-swollen and water-swollen membranes with regard to W_{DSC} and W_{non}. The change in the permeability through the membranes was not correlated quantitatively with that in the amount of each state of water in the membranes. The solutes difficult to permeate through the membranes showed higher activation energies. The specific interaction between the membrane substrates and solutes must be considered.

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