

Permeability through Cellulose Membranes Grafted with Vinyl Monomers in a Homogeneous System. VI. States of Water in Membranes Swollen in Solutions

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Synopsis

Cellulose grafted with vinyl monomers in a dimethyl sulfoxide–paraformaldehyde solvent system was used as membrane materials. The states of water in the membranes swollen in aqueous solutions of NaCl, raffinose, and poly(ethylene glycol) (PEG) were investigated. The amounts of total water and freezing water for the solution-swollen membranes hardly depended on the kind of solutions and were similar to those for the water-swollen membranes. The free water contents for the solution-swollen membranes were different from those for the water-swollen membranes. Apparent activation energies for diffusive permeation of solutes through the membranes were measured. A poor permeability of PEG through the membranes was consistent with a large activation energy for permeation of PEG through them.

INTRODUCTION

It has been reported^{1–15} that different states of water are present in water-swollen membranes. The amount of each state of water in membranes depends on the affinity of membrane substrates for water. In a series of studies,^{16–20} we have used cellulose grafted with vinyl monomers in a dimethyl sulfoxide (DMSO)–paraformaldehyde (PF) solvent system as membrane materials. The kind of monomers and composition of copolymers were varied to prepare the membranes of different affinity for water. Diffusive permeation of solutes through these grafted cellulose membranes was discussed in relation to the states of water in them. However, the change in the permeabilities of solutes through the membranes was not correlated quantitatively to that in the amount of each state of water in them.

In our previous studies,^{16–20} the states of water were measured by the use of the membranes swollen in pure water. It has been reported^{21–24} that the amounts of total water and bound water, which is the water molecules bound to polymer molecules through hydrogen bonding, depend on the permeating solutes. In this paper, the states of water in the membranes swollen in solutions are investigated.

EXPERIMENTAL

Materials

Homogeneous grafting of vinyl monomers onto cellulose was carried out in a DMSO–PF solvent system by the method described previously.^{25–28} Acrylo-

nitrile (AN)-, methyl acrylate (MA)-, and 2-hydroxyethyl methacrylate (HEMA)-grafted cellulose membranes prepared in the previous studies^{16,18,20} were used for this study. Characterization of each membrane has been indicated in the previous papers.^{16,18,20} The commercial regenerated cellulose membrane, Cuprophan, and the membrane cast from the DMSO solution of cellulose, designated as the cellulose membrane, were also used.¹⁶

Diffusive Permeability

The permeability coefficients of solutes, P , were measured at given temperatures from 20.0 to 50.0°C by the method described in the previous paper.¹⁶ Several solutes of different molecular weight were used. The viscosity-averaged molecular weights for three commercial poly(ethylene glycol) (PEG) samples were estimated from the intrinsic viscosities obtained with benzene at 25.0°C.²⁹ The PEG samples were abbreviated as PEG-IV, PEG-VI, and PEG-XX in the order of increasing molecular weight.

Hydraulic Permeability

The hydraulic permeability of water was measured at given temperatures with a reverse osmosis batch cell (Fuji Seiki FMD300) having a volume of 300 cm³ and an effective membrane area of 24.6 cm².

Differential Scanning Calorimetry (DSC)

The states of water in the membranes were investigated with a Seiko SSC/560 DSC. The membranes were immersed in aqueous solutions of NaCl, raffinose, and PEG-VI for several days, wiped off surface water with paper, and 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⁻¹ 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 solute molecular weight dependence of permeability for various kinds of membranes is summarized in Figure 1. For other details the previous papers^{16,18,20} should be referred to. The molecular weight dependence of permeability for vinyl monomer-grafted cellulose membranes is different from that for cellulosic membranes and depends also on the kind of monomers. The permeabilities of intermediate molecular weight solutes through the grafted cellulose membranes are superior to those through the cellulosic membranes. The permeabilities of lower molecular weight solutes through the HEMA-grafted membrane (*g*-PHEMA 2) are better than those through the Cuprophan membrane, but the permeabilities of PEG samples are reversed. The permeabilities of lower molecular weight solutes through the AN-grafted membrane (*g*-PAN 3) and MA-grafted membrane (*g*-PMA 4) are almost on the similar level, but the permeabilities of PEG samples differ considerably.

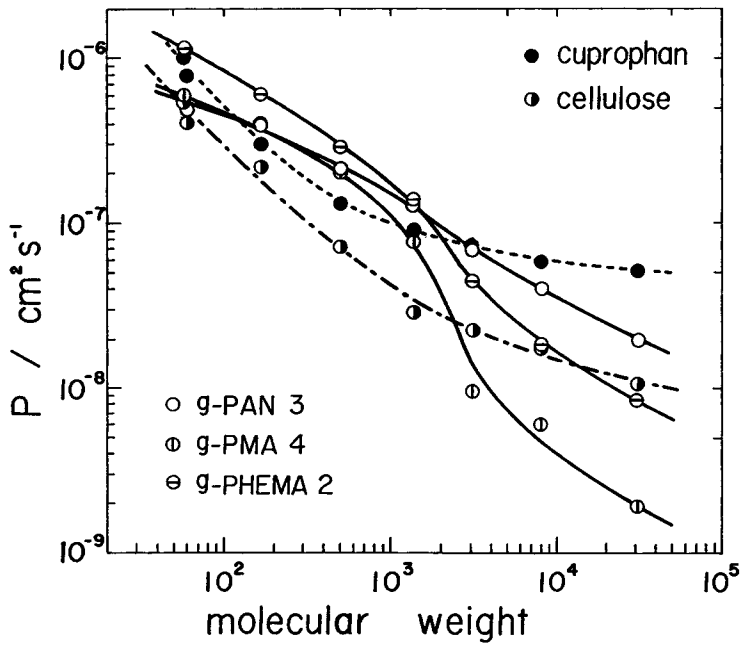


Fig. 1. Solute molecular weight dependence of diffusive permeability at 30°C for various kinds of membranes: (●) cuprophan; (●) cellulose; (○) *g*-PAN 3; (⊙) *g*-PMA 4; (⊖) *g*-PHEMA 2. The solutes are, in the order of increasing molecular weight, NaCl, urea, uric acid, raffinose, vitamin B₁₂, PEG-IV, PEG-VI, and PEG-XX.

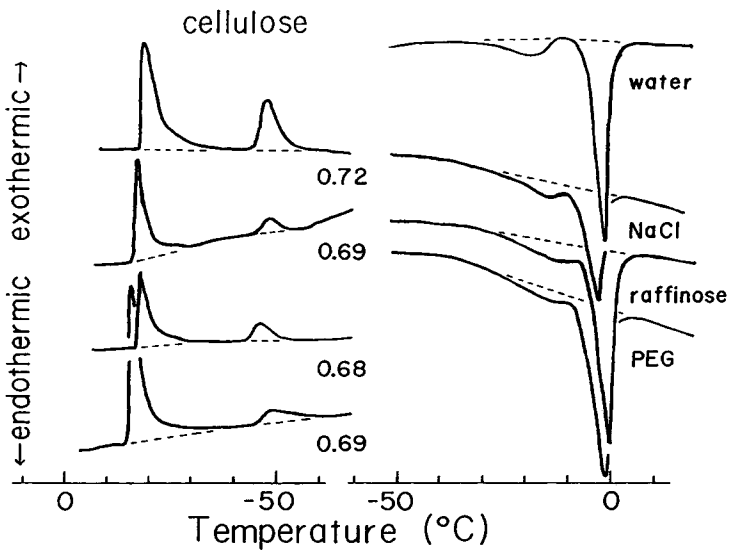


Fig. 2. DSC freezing and melting thermograms for the cellulose membranes swollen in water and aqueous solutions of NaCl, raffinose, and PEG-VI. Numbers on the curves give water content.

Figure 2 shows the freezing and melting thermograms for the cellulose membranes swollen in pure water and three kinds of aqueous solutions. Several peaks are found on both sets of thermograms, indicating the presence of several states of freezing water. The peaks at higher and lower temperatures, on the both thermograms, are assigned to free water and water interacting weakly with polymer molecules, intermediate water, respectively.¹⁷ The nonfreezing water which does not freeze even when cooled down far below the freezing point is assigned to bound water¹ and is thought to be less capable of dissolving solute.^{30,31} The peak temperatures for the solution-swollen membranes differ from those for the water-swollen membrane. On the exothermic curves, the free water peaks for the solution-swollen membranes shift toward higher temperatures but the intermediate water peaks hardly shift. On the endothermic curves, the free water peaks shift toward lower temperatures but the intermediate water peaks shift toward higher temperatures. These results indicate that there is a difference between the freezing and melting processes with regard to the influence of solutes on the phase transition temperatures of water in the membranes. The distinction between freezing and melting behaviors has been also recognized for the water-swollen membranes.^{6,14,17-19} The investigation of both thermograms is important to understand the states of water in membranes more precisely.

The DSC thermograms for the *g*-PHEMA 2 membranes are indicated in Figure 3. The influence of grafted PHEMA chains is evident; the exothermic peaks at around -50°C and the endothermic peaks at -20°C disappear but endothermic peaks appear at around -10°C . It is clear that the intermediate water peaks for the solution-swollen membranes are influenced. The other grafted cellulose membranes also indicated the influence on the intermediate water peak.

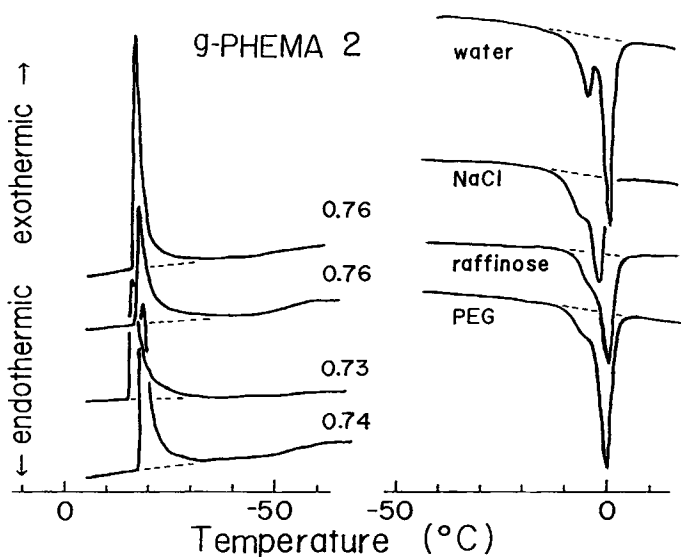


Fig. 3. DSC freezing and melting thermograms for the *g*-PHEMA 2 membranes swollen in water and aqueous solutions of NaCl, raffinose, and PEG-VI. Numbers on the curves give water content.

Figure 4 reveals the relationship between the water content and heat of fusion of freezing water, ΔH , determined from the area under the endothermic peaks. The data points for each solution-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 4, thus, implies that the amount of nonfreezing water decreases at lower water contents. A similar result has also been reported for other membranes.^{3,4,17-20} The equilibrium nonfreezing water content was estimated by extrapolation of the straight part to $\Delta H = 0$. The equilibrium freezing water content was calculated from the difference between the equilibrium nonfreezing water content and equilibrium water content determined by the method described in the previous papers.¹⁷⁻²⁰ As can be seen from Figures 2 and 3, the endotherms can be resolved roughly into each state of water. The results are listed in Table I. The data for water-swollen membranes^{17,18,20} are also listed. There is little difference among the membranes swollen in pure water and solutions with regard to the water content and nonfreezing water content. However, the proportion of free water differs from one another. The free water contents for the solution-swollen cellulosic membranes are less than those for the water-swollen ones. The free water contents for the AN- and HEMA-grafted cellulose membranes swollen in the solutions increase but those for the MA-grafted membranes decrease.

It has been reported^{3,32} that certain solutes can permeate nonfreezing water regions in membranes. The difference in solute permeable water regions must be considered.^{7,11,32-34} The amount of each state of water in the solution-swollen membranes is drawn in Figure 5. Among these membranes, the amounts of total water and freezing water for the Cuprophan membrane are the largest, but with respect to free water the amount for the *g*-PAN 3 membrane is the largest. Moreover, the freezing water content for every grafted cellulose mem-

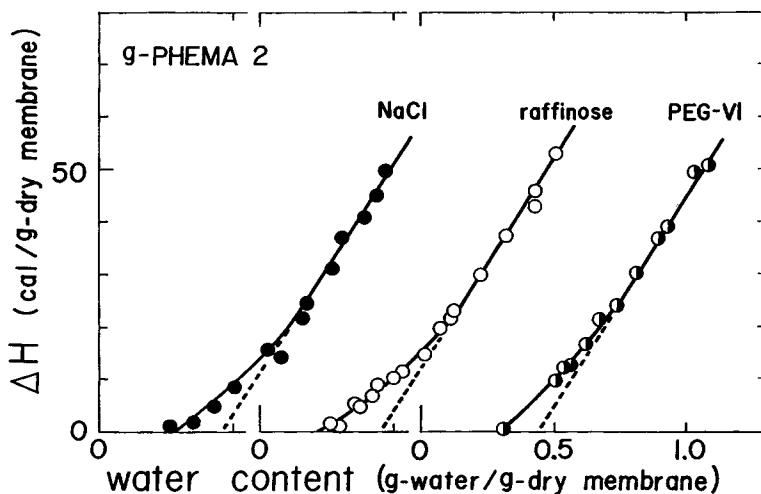


Fig. 4. Total water content dependence of the heat of fusion of freezing water for the *g*-PHEMA 2 membranes swollen in aqueous solutions of NaCl (●), raffinose (○), and PEG-VI (●).

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

Sample	Equilibrium water content	Equilibrium nonfreezing water content	Equilibrium freezing water content		
			Overall	Free water	Intermediate water
(wt of water in membrane/wt of dry membrane)					
Cuprophane					
Water	1.00	0.49	0.51	0.24 (46%)	0.27 (54%)
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%)
<i>g</i>-PAN 3					
Water	0.60	0.32	0.28	0.22 (78%)	0.06 (22%)
NaCl	0.60	0.30	0.30	0.26 (87%)	0.04 (13%)
Raffinose	0.60	0.32	0.28	0.24 (87%)	0.04 (13%)
PEG-VI	0.60	0.32	0.28	0.25 (88%)	0.03 (12%)
<i>g</i>-PMA 4					
Water	0.62	0.33	0.29	0.22 (74%)	0.07 (26%)
NaCl	0.61	0.33	0.28	0.18 (64%)	0.10 (36%)
Raffinose	0.61	0.32	0.29	0.18 (61%)	0.11 (39%)
PEG-VI	0.60	0.33	0.27	0.18 (66%)	0.09 (34%)
<i>g</i>-PHEMA 2					
Water	0.77	0.46	0.31	0.22 (71%)	0.09 (29%)
NaCl	0.76	0.46	0.30	0.23 (77%)	0.07 (23%)
Raffinose	0.75	0.45	0.30	0.23 (78%)	0.07 (22%)
PEG-VI	0.74	0.44	0.30	0.25 (82%)	0.05 (18%)

brane is about 0.30. The proportion of free water for each membrane scarcely depend on the kind of the solutions immersed. Comparison of Figure 5 with Figure 1 indicates that the order of permeability of each solute through the membranes does not correspond to the amount of any state of water. It is difficult to explain 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 diffusive permeation of solutes and hydraulic permeation of water through the membranes are listed in Table II. The previous data^{19,20} are also indicated. Activation energy is thought to be a measure indicating the extent of an interaction between solute and membrane substrate. Activation energies for permeation of NaCl and urea through the *g*-PAN 3 and *g*-PMA 4 membranes are slightly larger than those through the cellulosic membranes. Moreover, activation energies for PEG-VI through the grafted cellulose membranes are obviously large. These results are consistent with poor permeabilities of these solutes through the grafted cellulose membranes shown in Figure 1. A similar specific interaction has been reported on the permeabilities

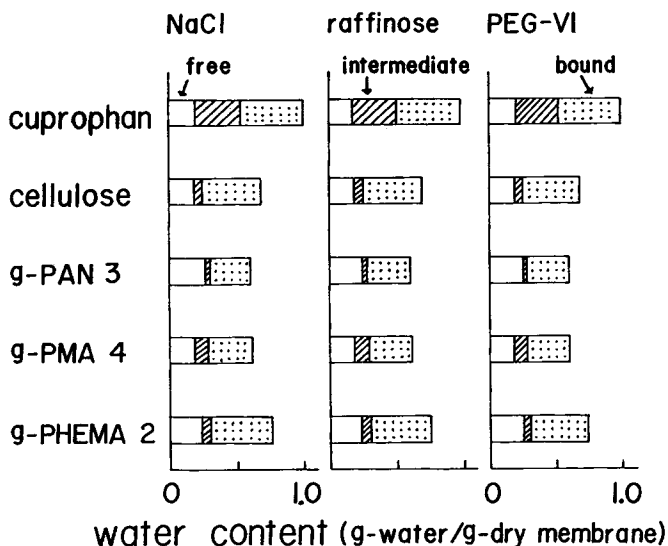


Fig. 5. Amount of each state of water in various membranes swollen in aqueous solutions of NaCl, raffinose, and PEG-VI: (□) free water; (▨) intermediate water; (◻) bound water.

of vitamin B₁₂ and PEG through methyl methacrylate (MMA)-grafted cellulose membranes.¹⁹ On the other hand, activation energies for hydraulic permeation of water through all kinds of membranes are similar to that for purely viscous flow of water through a rigid capillary.³⁵ The difference in the proportion of each state of water hardly influences activation energy for water through the membranes. However, it has been reported¹⁹ that activation energy for water through the MMA-grafted cellulose membrane, whose fraction of nonfreezing water is more than 70%, is a few times larger than those listed in Table II. The participation of hydrophobic hydration water was suggested.^{36,37}

In this paper, the diffusive permeabilities of solutes through the membranes were discussed in relation to the amount of each state of water in the membranes swollen in the solutions. The free water contents for the solution-swollen membranes were different from those for the water-swollen membranes. However, the difference in the molecular weight dependence of permeability was not

TABLE II
Apparent Activation Energy for Diffusive Permeation of Solute
and Hydraulic Permeation of Water

Solute	Apparent activation energy (kcal mol ⁻¹)				
	Cuprophane	Cellulose	<i>g</i> -PAN 3	<i>g</i> -PMA 4	<i>g</i> -PHEMA 2
NaCl	4.3	4.2	4.4	4.6	3.9
Urea	3.8	4.3	4.8	4.8	4.2
Uric acid	4.6	4.8	4.2	4.3	4.5
Raffinose	4.6	5.1	4.2	4.3	5.0
Vitamin B ₁₂	4.4	5.0	4.1	4.4	4.9
PEG-VI	3.2	3.2	6.4	7.4	5.5
Water	4.2	3.6	3.8	3.8	3.9

explained quantitatively by that in the amount of each state of water. A poor permeability of PEG through the grafted cellulose membranes was consistent with a higher activation energy for permeation of PEG through them. The explanation for better permeabilities of intermediate molecular weight solutes through the grafted cellulose membranes is not clear at the present stage.

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Received July 5, 1989

Accepted August 9, 1989