The States of Water in Cellulose Acetate Membranes

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Synopsis

Differential scanning calorimetric melting endotherms of wet and half-dried cellulose acetate membranes and salt distribution coefficients were studied to clarify the states of water in membranes. We have suggested that (a) there are four states of water in cellulose acetate membranes; (b) these states of water are those of completely free water, free water very weakly interacting with polymer, bound water which can contain salts, and bound water which rejects salts; (c) the semipermeability of membranes depends on the ratio of four states of water in membranes.

INTRODUCTION

There are a number of studies on the states of water in cellulose acetate membranes which act as selective membranes in the separation of water from salt solution by reverse osmosis. An understanding of the properties of water in cellulose acetate membranes seems to be highly important for making clear the mechanism of the semipermeability of membranes.

Magne et al.[1,2] have suggested "nonfreezing water" and have offered some explanation for this water in connection with the interaction between water and cellulose. In the recent studies based on nuclear magnetic resonance (NMR), it has been suggested that a significant fraction of the water in various cellulose acetate membranes is the "nonfreezing water," namely, "adsorbed water."[3] On the other hand, there is a study based on thermodynamic data.[4]

The technique of differential scanning calorimetry (DSC) has been employed for a study of nonfreezing water.[5] It has been clarified by these experimental techniques that the amount of nonfreezing bound water depends on membrane morphology, increasing with decrease in the packing density of the polymer within the membrane, and all the water contained in dense membranes is bound to the polymer. However, inquiry with regard to the influence of bound water on the semipermeability of membranes has not been fully scrutinized.

In this paper, we have suggested that (a) there are four states of water in cellulose acetate membranes; (b) the semipermeability of membranes depends on the ratio of four states of water in the membranes.

EXPERIMENTAL

Skinned and Dense Membrane Preparation

The cellulose acetate (CA) used in this study was Eastman's Type E-398-3. Acetone and formamide of spectrograde purity were used.

The skinned asymmetrical membranes were prepared by the procedure essentially similar to that described by Manjikian.[6] In this case, the casting solution consisted of 25 wt-% CA, 45 wt-% acetone, and 30 wt-% formamide. The thin membranes cast on glass plates were allowed to evaporate at ambient atmosphere for 20 sec, and then were immersed in water at 4°C. These membranes were annealed in 80°C water for 15 min. These membranes were about 120 μm thick.

The dense membranes (~25 μm thick) were prepared by casting the binary solution consisting of 25 wt-% CA and 75 wt-% acetone on glass plates. The cast membranes were allowed to evaporate for one day, and then were immersed in water.

Differential Scanning Calorimetry of Wet Membranes

The membranes studied by DSC were wiped with filter paper to remove extra external water and then sealed in aluminum pans to prevent evaporation of water during the measurement. The sample size was about 2–4 mg. The differential scanning calorimeter employed here was Perkin-Elmer Type DSC-1B. The sealed pans were cooled to −30°C and then heated to 25°C at a rate of 4°C/min. The total water content of the membranes was determined from the weight loss after drying under vacuum at 60°C for 3 hr. The free (freezing) water content was determined from the area of melting endotherm concerned with the amount of freezing water. The bound (nonfreezing) water content was determined from the difference between the free water and total water content.

The total water content was varied in order to investigate the influence of the total water content on the states of water in the membrane. The adjustment of total water content was performed by allowing the membrane wrapped by filter paper to evaporate at ambient atmosphere for a suitable time.

Measurements of Salt Distribution Coefficients in Membranes

Each membrane was immersed in 4% aq. NaCl solution for two days, and then wiped with filter paper to remove extra external solution. After immersing it in distilled water for two days, the distribution coefficient $K*$ was calculated from the NaCl concentration of the solution determined by conductivity measurements. $K*$ is defined here as the ratio of NaCl concentration of aq. solution in the membrane to that of external solution; therefore it follows that

$$K* = \frac{(W_s/W_w)_m}{(W_s/W_w)_e}$$

where W_s and W_w are salt and water weight, respectively, and subscripts m and e are membrane and external solution phase, respectively.

RESULTS AND DISCUSSION

Typical melting endotherms of pure water and water in the wet-skinned membranes are shown in Figures 1d and 1a. The areas of the melting peaks
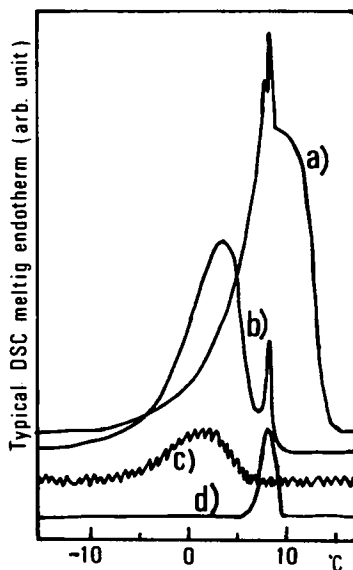
Fig. 1. Typical DSC melting endotherms of water in membranes and of pure water: (a) 57.6%; (b) 32.6%; (c) 14.5% total water contents; (d) pure water.

given in this figure were reproducible to 3–4% on repeated runs. But the melting temperature values deviated about 5–8°C from the true values. However, such a deviation does not affect any of the arguments and conclusions given below. Comparing the shapes of the melting peaks of the skinned membrane with that of pure water, it is noticed about the skinned membrane that (a) the peak starts at 10–15°C lower than that of pure water; (b) the shape of the peak consists of sharp and broad components. These results indicate that there are various states of water in skinned membranes. For making clear the states of water in the membrane, the melting endotherms of water in the membranes adjusted to various total water contents were measured, and are shown in Figures 1b and 1c. The sharp component of the peak in Figure 1a holds the same temperature value (near 8°C) as that in Figure 1b, but the broad component of the peak shifts toward the low-temperature region with decrease in total water content. No sharp component of peak appears in Figure 1c.

It seems from the above experimental results that (a) the sharp component of the peak near 8°C is completely free water; (b) the broad one is assigned to the free water very weakly interacting with polymers, probably the interaction of water and capillaries of polymer. The sharp component of the peak is more sensitive than the broad one for decrease in total water content in membranes. And then, the sharp component corresponding to the completely free water is not recognized in the membrane which contains total water less than 15–18%.

The melting point of the free water very weakly interacting with polymers shown in Figure 1 shifts toward the low-temperature region with decrease in the total water content. It seems that there are two causes for this shift. Firstly, it is reported[7] that the structure of this water is broken by the interaction with polymers. For this reason, the entropy change of melting of this
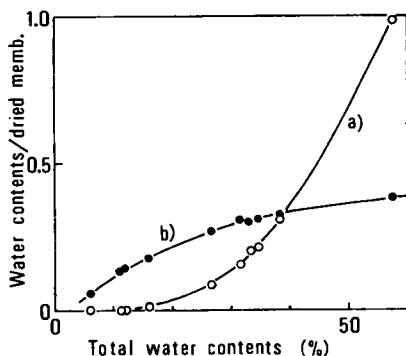
Fig. 2. Dependence of free water and bound water contents on total water contents in skinned membranes: (a) free water; (b) bound water.

water is larger than that of completely free water; and consequently, the melting point of this water shifts toward the low-temperature region with decrease in the total water content. Secondly, in the free water very weakly interacting with polymer defined above, there would exist water which differs in interaction with polymer, namely, from relatively weakly interacting water to relatively strongly interacting water. The amount of the relatively weakly interacting water component decreases faster than that of the relatively strongly interacting water component with decrease in the total water content, and then the ratio of the relatively strongly interacting water component increases. Consequently, the melting point of this water shifts toward low temperature to all appearances.

The bound (nonfreezing) and free (completely and very weakly interacting) water contents were estimated and are shown in Figure 2. One notices in Figure 2 that the free water content decreases faster than the bound water content with decrease in the total water content, and that the free water content is zero in the skinned membrane containing about 12–13% total water content. It is also noticed that the bound water component simultaneously decreases with decrease in the free water component. In other words, this does not mean that the bound water starts to decrease after the free water does not exist at all. This result probably indicates that each state of water in the membrane is not fixed and that the water molecules in each state are exchangable with each other.

Typical melting endotherms of water in dense membranes were measured. But no peak of typical melting endotherms was obtained by DSC measurment. Consequently, all water is bound water in the dense membrane containing about 10% total water content.

TABLE I
Water Contents and Distribution Coefficients of Skinned and Dense Membranes

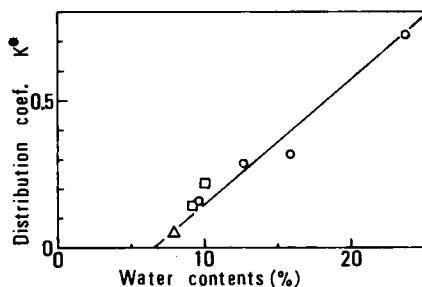| Membrane	Water content, %	Distribution coefficient K^*
Skinned	63.8	1.0
Dense	10.0	0.22

Fig. 3. Relation between salt distribution coefficient and total water content in dense membranes: (□) diacetate membrane; (△) triacetate membrane (prepared from Daiseru's triacetyl cellulose type LT-70); (○) Lonsdale's data.[8]

Distribution coefficients $K*$ of NaCl in membranes are shown in Table I. The skinned membrane mainly consists of a porous layer which does not contribute to the semipermeability, therefore it is probable that $K*$ of the skinned membrane is unity. This result indicates that the free water in the membrane does not contribute to the semipermeability of membranes. But it seems that the bound water plays an important role in this property. Namely, the oriented bound water may have no ability to solvate ions, consequently rejects the ions. But the water molecules are able to diffuse through the bound water phase. Under actual conditions, all bound water which is distinguished from free water by DSC measurment is not able to reject ions. The distribution coefficient $K*$ of NaCl is 0.22 in the dense membrane where all water is in the bound state.

If we suppose that bound water could be divided into bound water which can contain salts and bound water which rejects salts (we call it "completely bound water"), it seems that the completely bound water content is 78% of total water content in dense membranes. This result indicates that if we could make the membrane containing about 7.8% total water, the salt distribution coefficient of this membrane would be nearly zero. On the other hand, the relation between salt distribution coefficients and total water content in various cellulose acetate membranes is shown in Figure 3. One could estimate by extrapolation of the line in Figure 3 that if the membrane contains 6–7% total water, $K*$ would be nearly zero, namely, this membrane could perfectly reject ions. This water content is in agreement with the above results estimated from the salt distribution coefficient of the dense membranes.

Dense membrane is roughly similar to an active dense layer of skinned membrane. Consequently, the previous discussion concerning dense membrane may be extended to active layers of skinned membranes.

The ratio of water content of each state closely depends on the structure of the membranes. It seems that the ratio of bound water is smaller in the membrane containing large pores than in the membrane containing small pores. The relation between distribution of pore size and the ratio of free water very weakly interacting with polymer to completely free water is similar to the previous one. Consequently, one may be able to estimate distribution of pore size in skinned membranes by a further study on the four states of water in membranes.

CONCLUSIONS

The experimental observations presented above suggest that:

1. There are four states of water in cellulose acetate membranes.

2. These states of water are those of completely free water, free water very weakly interacting with polymer, bound water which can contain salts, and bound water which rejects salts.

3. Completely free water, free water very weakly interacting with polymers, and bound water components in skinned membrane decrease simultaneously with decrease in total water content.

4. Completely free water vanishes in skinned membrane with less than 15–18% total water content.

5. Free water very weakly interacting with polymers vanishes in membranes with less than 12–13% total water content.

6. Bound water which can contain salts vanishes in membranes with less than 6–7% total water content, and there is only bound water which rejects salts in the membrane.

7. The larger the ratio of completely bound water is, the better the semipermeability of the membrane.

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