

Water Binding and Irreversible Dehydration Processes in Cellulose Acetate Membranes*

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Synopsis

The relative amounts of freezing and nonfreezing water in various water-wet cellulose acetate (CA) membranes were determined by NMR techniques, from the initial heights of the water component in the free induction decay (MNR intensity). The results suggest that (1) a significant fraction of the water in various wet CA membranes does not freeze, probably because of strong interaction with the polymer; (2) the relaxation times T_2 of the nonfreezing water are of the order of milliseconds indicating that they are still highly mobile compared with ice; (3) all the water contained in dense CA films or in membranes equilibrated at relative humidity of 0.93 does not freeze upon cooling the membranes from room temperature to -60°C ; (4) the amounts of nonfreezing bound water in membranes is higher than the total amount of water absorbed from liquid water by a dense film of the same polymer. However, the amounts of nonfreezing water in various CA membranes as calculated from the "relative NMR intensities" is substantially lower than those calculated from DSC melting endotherms by assuming the heat of fusion of water in membranes to be identical to that of pure water. Various possible reasons for this discrepancy are discussed. Measurements on the first desorption-adsorption cycle of *wet* CA membranes have also been performed. They suggest that during the first dehydration process, irreversible changes are induced in the structure of the membrane which result in a significantly lower accessibility of the polymer to interact with water. The extent of these irreversible changes in membrane structure is dependent on the details of the dehydration process being more pronounced at higher temperatures.

INTRODUCTION

In a recent study on "Freezing and Non-Freezing Water in Cellulose Acetate Membranes," based on differential scanning calorimetric (DSC) and on scanning electron microscopic data,¹ it has been suggested that (1) a significant fraction of the water in various wet cellulose acetate membranes does not freeze, probably because of strong interaction with the polymer; (2) the amount of nonfreezing (bound water) depends on membrane morphology, increasing with the decrease in the packing density

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(compactness) of the polymer within the membrane; (3) all the water contained in dense polymeric films is bound to the polymer and does not freeze. (The term "bound water" used in this article should not be confused with "structured" or "ice-like" water. This is clearly indicated by the NMR data given below.)

These conclusions have now been tested by NMR techniques, and quantitative estimates of the amounts of nonfreezing water in various wet CA membranes have been made.

Measurements on the first desorption-adsorption cycle of *wet* CA membranes have also been performed. They suggest that during the first dehydration process, irreversible changes are induced in the structure of the membrane which result in a significantly lower accessibility of the polymer to interact with water.

EXPERIMENTAL

Materials and Membrane Preparation

The cellulose acetate (CA) used in this study was Eastman's type E-398-10. Acetone and dimethyl sulfoxide were of analytical-grade purity, whereas the triethyl phosphate was of practical grade.

Membranes were cast from 20% (weight) polymer solutions. A thin (~ 0.3 mm) film of CA solution was cast at ambient temperature, on a glass plate, and precipitated in an ice-water bath. All membranes were annealed in a water bath at 80°C or at 95°C for 30 min and stored in water until use.

The dense CA film was cast from 20% CA in acetone and evaporated to dryness at ambient conditions (~ 24 hr). This dense film was then soaked with water for at least 48 hr prior to its testing. The detailed preparation procedure of the membranes used in this study are described in Table I and in the coding of the membranes.

Membranes are coded according to their preparation procedure. The first letters stand for the type of polymer used (CA = cellulose acetate).

TABLE I
Preparation Procedures of the Various CA Membranes
Used in This Study

Membrane no.	Type of membrane	CA in casting solution, %	Casting solvent	Air exposure period	Temp. of annealing bath, °C
1	CA-20-T-IL-80	20	triethyl phosphate	none	80
2	CA-20-T-IL-95	20	triethyl phosphate	none	95
3	CA-20-S-IL=80	20	dimethyl sulfoxide	none	80
4	dense films	20	acetone	~ 24 hr	~ 23

The next two figures represent the concentration, expressed in weight per cent, of the polymer in the casting solvent; triethyl phosphate (T) or dimethyl sulfoxide (S). The air exposure period between casting and immersion in water is described in the next two letters, IL standing for immediately leached. The last two figures in the code describe the temperature ($^{\circ}\text{C}$) of the water bath in which membranes were annealed for 30 min.

The membranes are distinguished also according to their handling *after* their preparation. We shall distinguish later on between three types of CA-20-T-IL-80 membranes; a membrane which was wet when tested and only blotted from extra external water, a membrane which was equilibrated at room temperature with water vapors at 90% relative humidity, and a membrane which was freeze-dried and then equilibrated at 90% relative humidity.

The reverse osmosis properties of the membranes used in this study, as well as detailed analysis of their structures, and other data on their properties have been given in earlier publications.¹⁻³ It has been shown¹ that the properties of water in CA membranes cast from the standard (ternary) Loeb-Sourirajan solution can be explained by the same principles which explain their properties in CA membranes cast from binary solution.

NMR Measurements

In the NMR experiment, the free decay following a 90°C pulse was examined at different temperatures. Generally, the *initial height* (at zero time after the pulse) of the free decay is proportional to the *total* amount of protons in the examined sample.⁴ In our samples, the free decay consists of a very fast component ($T_2 \simeq 30\text{--}50 \mu\text{sec}$) characteristic of proton decay in solids (e.g., solid polymer or a frozen liquid), and a slow-decaying component (of the order of 1 msec and longer) which is probably due to the *mobile* water molecules. If a slow decay is observed below the freezing point, its extrapolated height to zero time after the 90° pulse should be proportional to the amount of *unfrozen* water. In our experiments, we have extrapolated the *slow-decaying component* in the free induction decay to zero time and estimated the amount of mobile water protons in various membranes from the extrapolated initial height. This extrapolated initial height of the slow-decaying component will be abbreviated later on as "NMR intensity."

Desorption-Adsorption Studies

The desorption-adsorption studies were performed at room temperature ($\sim 21^{\circ}\text{C}$), with a circulatory water vapor sorption apparatus⁵ shown in Figure 1. It uses air as the carrier gas and, in its circulatory path, passes from the pump through a saturated salt solution which fixes the relative humidity.

From here, the gas-vapor mixture passes upward through the sample tube where equilibration takes place and then back to the pump to complete the cycle. A peristaltic pump with plastic tubing assures that the

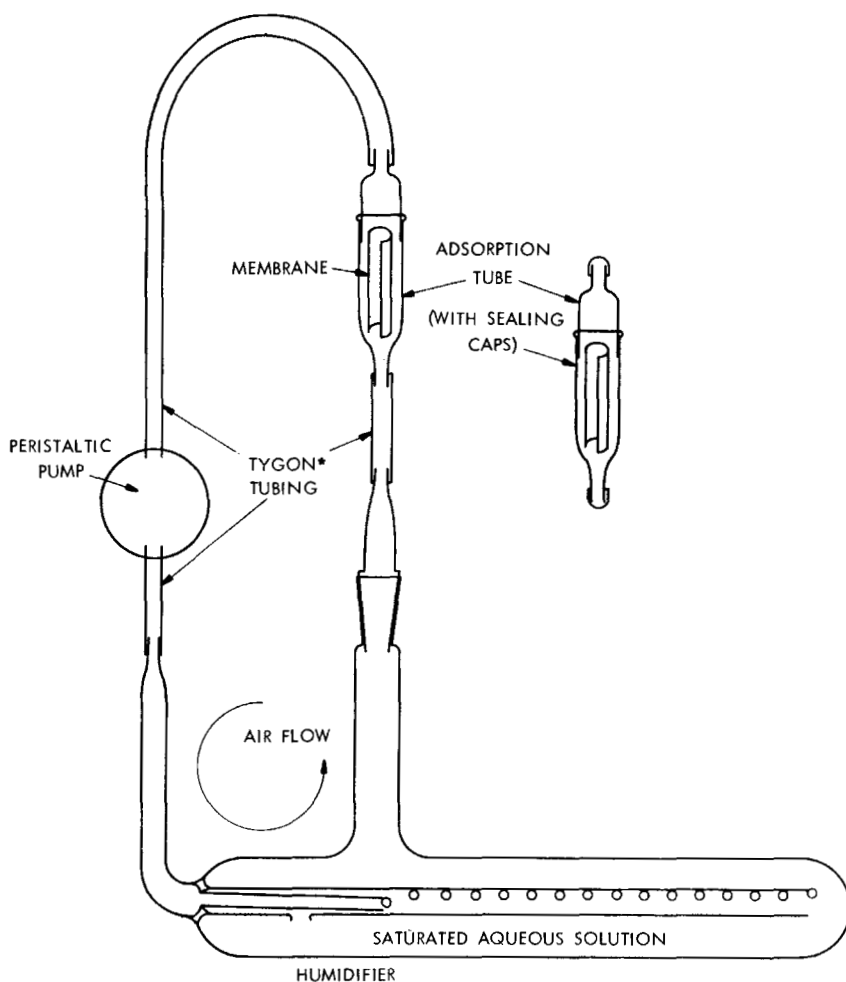


Fig. 1. Circulatory water vapor sorption apparatus (Ref. 3).

circulating vapor contacts no metal, valves, or foreign lubricants and its total volume is kept desirably small. Once a day, the sample tubes are capped at both ends and the assembly weighed.

RESULTS AND DISCUSSION

NMR Evidence for the Existence of Nonfreezing Bound Water in Wet CA Membranes and for Irreversible Dehydration Processes in These Membranes

The free induction decay of a wet CA-20-T-IL-80 membrane at various temperatures is shown in Figure 2. (As explained in the experimental section, there are three types of CA-20-T-IL-80 membranes which are distinguished according to their handling after preparation.) A dramatic

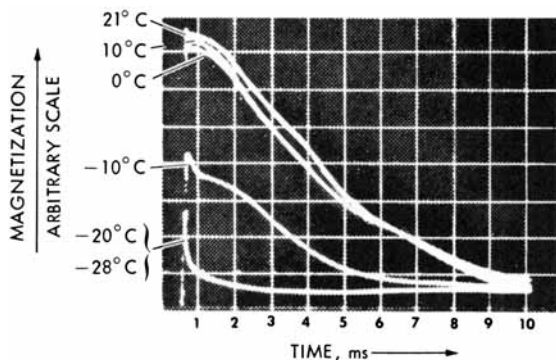


Fig. 2. Free induction decay of a wet CA-20-T-IL-80 membrane at various temperatures.

decrease in the height of the free induction decay signal occurs while cooling from 0°C to -20°C demonstrating freezing of most of the water. The lowering of the initial height of the free decay signal (NMR intensity) upon cooling from -10°C to -20°C is consistent with the supercooling effects and lowering of the melting temperature observed also in our differential scanning calorimetric studies of this system.¹ The following relative heights of the free induction decay trace were observed as a function of temperature in the course of heating a frozen CA-20-T-IL-80 wet membrane.

	-8°C	-6°C	-2°C	0°C	+2°C
Relative NMR intensity	10	12	22	35	70

At -2°C, the above intensity was obtained within 10 min. Temperature was then kept constant for 1 hr, and no further change was observed. The most important conclusion suggested by the data shown in Figure 2 is that a nonnegligible fraction of the water contained in this membrane does not freeze and that this fraction is highly mobile compared with ice.

This conclusion is strongly supported by the data shown in Figure 3 describing the free induction decay of CA-20-T-IL-80 membranes equilibrated at room temperature with water vapors at 90% relative humidity. Sample A was freeze-dried before equilibration, while sample B only blotted from extra external water before equilibration.

It may be seen that each decay consists of a very fast component (30–50 μ sec), and a much slower component of the water. These experiments indicate that (a) no significant immobilization of the water molecules occurred upon cooling down to -40°C; and (b) the amount of water contained in a wet membrane equilibrated at room temperature with water vapors at 90% relative humidity is approximately twice the amount of water adsorbed on a freeze-dried membrane under identical equilibration conditions. (It is reasonable to expect that since the equilibration period was two weeks, equilibrium was attained.)

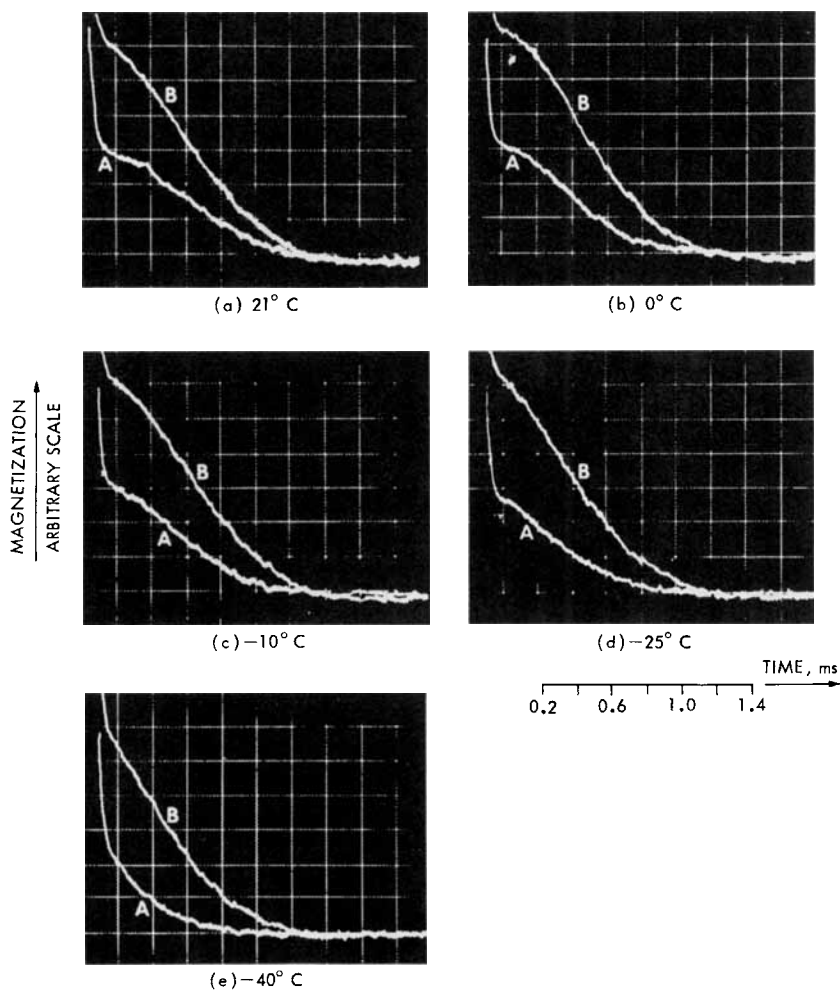


Fig. 3. Free induction decay of CA-20-T-IL-80 membranes equilibrated at room temperature with water vapors at 90% relative humidity. (Sample A was freeze-dried before equilibration while sample B only blotted from extra water before equilibration.)

Evidence for Irreversible Dehydration Processes in Wet CA Membranes from Desorption-Adsorption Isotherms

The observation that the amount of water contained in sample B of Figure 3 (which was only blotted from extra external water before equilibration at 90% relative humidity) was approximately twice that contained in sample A (which was freeze-dried before equilibration under identical conditions) is consistent with the observations reported¹ that the amount of nonfreezing (bound) water found in a wet membrane is significantly higher than the total amount of water adsorbed at 100% relative humidity

TABLE II
Water Contents and Distribution of Freezing and Nonfreezing Waters in
Various Wet CA-20-T-IL-80 Membranes as Estimated
From DSC Measurements¹

	Membranes stored in water since preparation	Freeze-dried and reimbibed in water
H ₂ O in Wet Membrane, %	71	34
Weight of Water, g per g dry CA	2.4	0.57
Fraction of nonfreezing H ₂ O from total water	0.30	0.83
Weight of Nonfreezing Water, g per g dry CA	0.72	0.42

by these same membranes after being dehydrated. Both observations suggest that when very loose cellulose acetate membranes are dehydrated, void collapse and thickening of the polymeric walls cannot be eliminated, even if the membrane is slowly freeze-dried. The lower amounts of water adsorbed on a dry membrane result from lower accessibility of the polymeric chains to binding water. This occurs because the extent of polymer-polymer interactions in the dry membrane is larger than in a wet one. This hypothesis is supported by measurements at room temperature of the first desorption-adsorption cycle.

The first desorption-adsorption cycle, at room temperature, of H₂O on a wet CA-20-T-IL-80 membrane is shown in Figures 4 and 4a, whereas the corresponding desorption-adsorption isotherms on CA-20-T-IL-95 are shown in Figure 5. It is important to notice that the amounts of water bound to the membranes at R.H. = 1.0 after they were once slowly dehydrated (the first desorption process was carried on during more than three weeks) are eight to ten times smaller than the water content of the original wet membranes, even though the membranes were imbided in liquid water for reequilibration at R.H. = 1.0.

The lowering of the water-binding capability of a CA-20-T-IL-80 membrane after being slowly freeze-dried can be demonstrated by the data given in Table II, obtained by independent DSC measurements (for detailed explanation of the method, see ref. 1). While the total water content of the freeze-dried and rewetted membrane (0.57 g H₂O per g dry CA) is about five times lower than that of the original one (2.4 g H₂O per g dry CA), the fraction of the (bound) nonfreezing water in that membrane (83%) is about three times larger (compared to 30% in the original membrane). The total water content of the freeze-dried and rewetted membrane (0.57 g H₂O per g dry CA) is larger than the total water content of the same type of membrane after being slowly dehydrated at room temperature (~0.21 g H₂O/g CA), but smaller than the nonfreezing water content in the original membrane (0.72 g H₂O/g CA). This indicates that,

while the extent of irreversible changes induced in the wet membrane during its first dehydration is dependent on the details of the conditions of that process (being considerably larger at higher temperatures), such irreversible changes cannot be eliminated even if most of the water is removed at liquid nitrogen temperatures. The water-binding capability of the polymer in the membrane is always lowered during dehydration, presumably owing to an increase in the extent of polymer-polymer interaction in the membrane matrix. These conclusions are in accordance with observations on irreversible changes induced in CA desalination membranes during dehydration at room temperature, and on the deterioration of the desalination characteristics of such membranes when improper drying procedures are employed.⁶

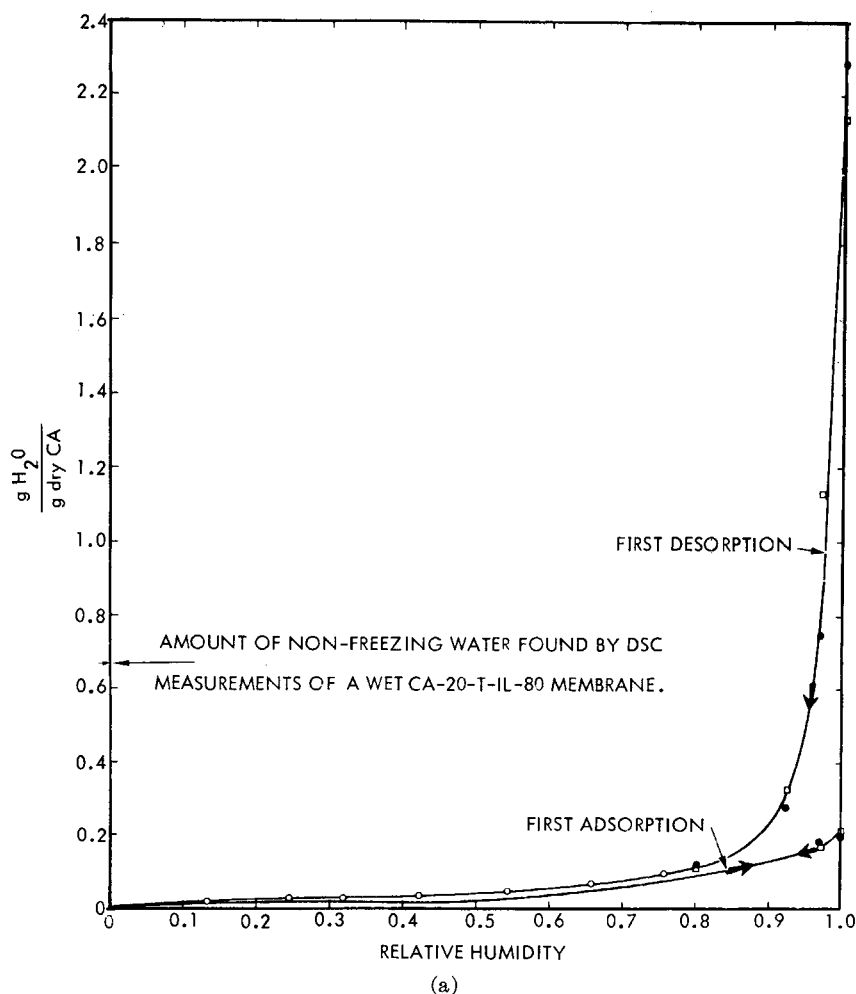


Fig. 4 (continued)

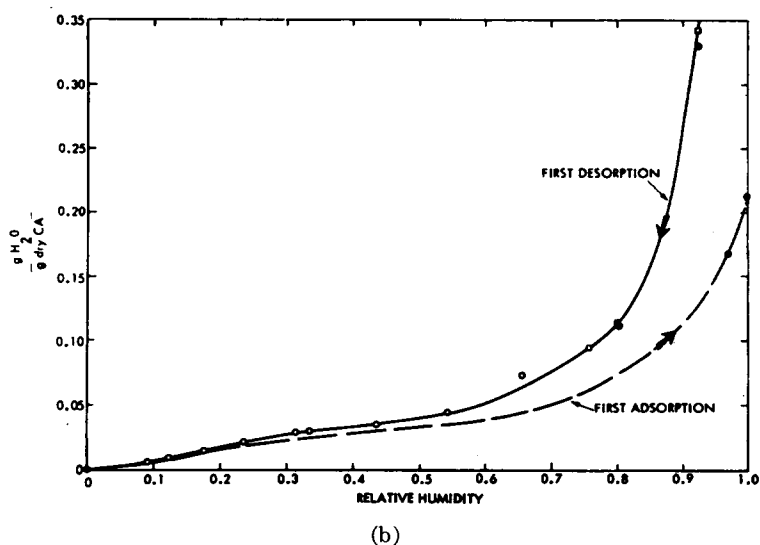


Fig. 4. (a) First description-adsorption cycle of H_2O on a wet CA-20-T-IL-80 membrane at room temperature ($\sim 22^\circ C$). Note: The amounts of H_2O bound to CA at R. H. = 1.0 have been determined after imbibing, or storing, the membrane in distilled water. (b) Details of the first description-adsorption cycle of H_2O on a wet CA-20-T-IL-80 membrane.

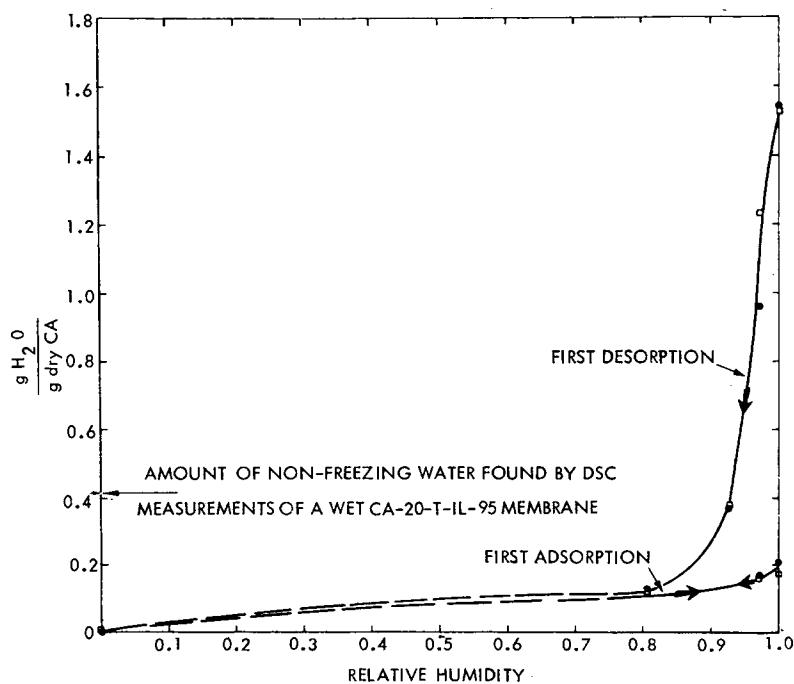


Fig. 5. First description-adsorption cycle of H_2O on a wet CA-20-T-IL-95 membrane at room temperature ($\sim 22^\circ C$). Note: The amounts of H_2O bound to CA at R. H. = 1.0 have been determined after imbibing, or storing, the membrane in distilled water.

An important practical implication of these observations is that the structures and the porosities of wet cellulose acetate membranes cannot be implied from adsorption isotherms of the dry membranes. It may be recalled that the pore size distribution in wet cellulose acetate desalination membranes had been deduced from the extra amount of water adsorbed into them as compared to the amount of water adsorbed by a dense film of the same material.⁷ The experimental evidence presented in this section for the occurrence of irreversible dehydration processes in wet cellulose acetate membranes suggests, however, that a better understanding of membrane structure and of water-polymer interactions might be gained through measurements of the first desorption process rather than that of water adsorption on a dry membrane.

Quantitative NMR Estimates of the Amounts of Nonfreezing Water in CA Membranes

As mentioned in the experimental section, the initial height of the slow-decaying component in the free induction decay (NMR intensity) is proportional to the total amount of mobile-water protons (as opposed to frozen-ice protons) in the sample. Comparison of the relative NMR intensities in various membranes can therefore serve as a measure of the relative amounts of mobile water in these membranes. Furthermore, since all the water contained in a "dense film" (see ref. 1) or in a membrane equilibrated at 90% relative humidity (see Fig. 3) is nonfreezing, it can be assumed that the NMR intensity at -10°C in such a membrane corresponds to the total amount of water. Therefore, these membranes were used as calibration samples for calculating the amounts of nonfreezing water in membranes which contain both freezing and nonfreezing water.

The "relative NMR intensities" at 25° and -10°C and the computed amounts of nonfreezing water in the various membranes for three CA membranes and for a "dense film" soaked with water are given in Table III. The results support the suggestion that the amount of nonfreezing (bound) water in CA membranes is higher than the total amount of water (all of which is nonfreezing) contained in a dense film from the same polymeric material which was soaked with water. However, the amounts of nonfreezing water in various CA membranes, as calculated from the "relative NMR intensities" at -10°C , are substantially lower than those computed from DSC measurements by assuming the heat of fusion of the freezing water to be identical to that of pure ice.¹ The average amounts of nonfreezing water calculated from repeated DSC measurements and from NMR measurements (using as references for calculating the amounts of nonfreezing water either a "dense film" soaked with water or a freeze-dried CA-20-T-IL-95 membrane equilibrated with water vapor at 0.90 R.H.) are summarized in Table IV. The discrepancies between the two types of estimations are far larger than the experimental error.

TABLE III
Relative Initial Heights of the Water Component in the Free Induction Decay
(Relative NMR Intensity) and Computed Amounts of Nonfreezing Water in
Various CA Membranes at 25°C and at -10°C

Type of membrane	Weight of dry membrane, mg	Water content, mg	Water content per g dry CA, g	Relative NMR intensity at 25°C	Relative NMR intensity at -10°C	Calcd. amt. of non-freezing H ₂ O g per g dry CA
CA-20-T-IL-80	110	262	2.38	100 ^a	100 ^a	0.24
CA-20-T-IL-95	83	162	1.95	60	66	0.20
CA-20-S-IL-80	82	232	2.83	91	71	0.22
Dense Film ^b	61	8.4	0.14		33	0.14

^a Arbitrary value.

^b Calibration sample.

TABLE IV
Average Amount of Nonfreezing Water in Various CA Membranes as Calculated
from the "Relative NMR Intensities"^a at -10°C and from DSC Measurements^b

Type of membrane	Nonfreezing Water, g per g dry CA	
	Calculated from relative NMR intensities at -10°C	Calculated from DSC measurements
CA-20-T-IL-80	0.22	0.70
CA-20-T-IL-95	0.18	0.41
CA-20-S-IL-80	0.19	0.53

^a Calculated from the relative initial heights of the water component in the free induction decay and the measured water content in a reference sample containing only bound nonfreezing water. (The reference samples used were dense CA films or a dried CA-20-T-IL-95 membrane equilibrated with water vapors at 90% R.H.)

^b Calculated from the DSC melting endotherms by assuming the heat of fusion of water in membranes to be identical to that of pure water.

Careful DSC measurements on a wet CA-20-T-IL-80 membrane which was equilibrated with water vapors at 93% relative humidity indicated that this membrane does not contain any freezing water. The total water content of this membrane is 0.31 g H₂O per g dry CA. This figure is higher than the ~0.22 g nonfreezing H₂O per g dry CA estimated for this membrane from NMR measurements. It suggests that the NMR estimates of the amounts of mobile water given in Tables III and IV for various CA membranes may be somewhat lower than the amounts of water which do not melt upon heating a prefrozen membrane. This may result from the existence of a highly nonmobile fraction in the nonfreezing water which, due to its very short NMR relaxation time, does not contribute to the NMR intensity of the "mobile" nonfreezing water. While the existence of such a fraction of highly nonmobile nonfreezing water has not yet been proved

in any system, and NMR studies on adsorbed water systems⁸ suggest that all the nonfreezing water is highly mobile compared with ice, the possible existence of such a fraction of highly nonmobile nonfreezing water may explain the discrepancy between the DSC and the NMR measurements and cannot yet be completely eliminated. In this context, it may be noted that the amounts of nonfreezing water in various membranes as estimated from the NMR intensities (Tables III and IV) are similar to the amounts of water adsorbed into these membranes at 100% R.H. after being dehydrated (Figs. 4 and 5).

On the other hand, the assumption that the heat of fusion of water in membranes is identical to that of pure bulk ice may also not be justified. A review of recent experimental tests of this assumption in various systems does not yield any conclusive results. Thus, while an independent NMR and DSC determination of the amount of nonfreezing water in collagen fibers indicated that the heat of fusion of the freezing water in that system is essentially that of pure water,⁸ and a similar behavior was assumed for water in a series of Hydrogel membranes,⁹ direct determination of the heats of fusion of water in wool keratin¹⁰ suggests that at low water contents, the heat of fusion of the freezing water is substantially lower than that of pure bulk ice. Thermodynamically, we have to expect a lowering of the heat of fusion which results from the lowering of the equilibrium freezing temperature. The magnitude of this effect as calculated from the Kirchhoff formula

$$\left(\frac{\partial \Delta H}{\partial T}\right) = \Delta C_p$$

is a decrease of ~ 9 cal/mole per 1°C decrease in the freezing temperature. Compared to the 1436 cal/mole heat of fusion, this is only a 0.6% decrease in the heat of fusion per 1°C . The lowering of the freezing temperature found experimentally was $5\text{--}15^\circ\text{C}$, and therefore the maximum decrease in the heat of freezing due to the lowering of the freezing temperature does not exceed 10%.

Lowering of the heat of fusion may also result from capillary and curvature phenomena. According to the Kelvin equation,

$$\ln P_0/P = \frac{2\bar{V}\gamma \cos \theta}{rRT},$$

vapors may liquify in capillaries having radius r at relative humidity P/P_0 lower than 1. In this equation, \bar{V} is the molar volume of the liquid, γ is its surface tension, θ is the contact angle of the liquid with the capillary walls, and R and T have their usual meaning. Utilizing this equation and assuming $\theta = 0^\circ$, one finds that a membrane equilibrated at 0.93 R.H. and 21°C may contain liquid water in capillaries having a radius of 130 \AA or lower. Freezing processes in such narrow capillaries may very well be associated with significant changes in the heat of fusion. Theoretically, the

changes in the heat of fusion can be calculated from the measured lowering of the freezing temperature, by equations such as

$$\ln \frac{T}{T_0} = - \frac{2}{\Delta H_f} \left[\frac{\bar{v}^S \gamma^{s,g}}{r^{s,g}} - \frac{\bar{v}^L \gamma^{l,g}}{r^{l,g}} \right]$$

or

$$\ln \frac{T}{T_0} = - \frac{2}{\Delta H_f} \frac{\bar{v}^S \gamma^{s,1}}{r^{s,1}}$$

or some combination of these equations,¹¹ depending on the curvatures of the solid and liquid interfaces (concave or convex) and on the type of interfaces involved. The practical application of these equations for calculating changes in the heat of fusion demands, however, detailed knowledge of the curvatures of the solid-liquid (namely, ice-water), solid-gas, and liquid-gas interfaces, as well as knowledge of the dependence of the various interfacial tensions on curvatures. Most of these variables are unknown (at the present time); and, therefore, thermodynamics cannot now be used for even estimating the extent of the changes in the heat of fusion.

In conclusion, it seems that the amounts of nonfreezing water in various CA membranes as estimated from DSC experiments (by assuming the heat of fusion of the freezing water to be identical to that of pure bulk ice) represent the upper limit for the amounts of "bound" water in these systems. The NMR data, which are consistent with the qualitative conclusions suggested by the DSC experiments, suggest that the amounts of nonfreezing bound water are lower than the estimates given in reference 1. Careful measurements of the dependence of the heat of fusion of the freezing water on the total water content in various membranes may resolve the reasons for the discrepancy between the two (DSC and NMR) methods.

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