

Studies on the Water in Cellulose Acetate Membranes by High Resolution ^1H NMR Spectroscopy

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Summary

High resolution ^1H NMR spectra of asymmetric and dense membranes of cellulose acetate were measured after immersing them in water, and two water peaks were observed. The upfield small peak was assigned to the bound water and the other to the free water. $^1\text{H-T}_1$ of the bound water was shorter than that of the free water. The bound water in the dense membrane is more strongly associated with the cellulose acetate surface than in the asymmetric membrane. The results were discussed in terms of the nature of the interaction forces working in water molecules and the properties of waters induced by such interaction forces.

Introduction

In reverse osmosis systems involving aqueous solutions, it has been established that both the chemical nature and the porous structure of the membrane surface have a governing influence on solute separations, which points out the importance of the nature of water at the membrane-solution interfacial region (SOURIRAJAN 1970). Consequently, it is of interest to study the state of water at the membrane-water interface for a fuller understanding of reverse osmosis transport.

In the literature several papers, in which the state of water contained in the membrane was studied by differential scanning calorimetry (DSC) (FROMMER, LANCET 1972; TANIGUCHI, Horigome 1975) or by nuclear magnetic resonance (NMR) techniques, (FROMMER, LANCET 1972; SUZUKI, ISHII 1972; YAMABE et al. 1972a; YAMABE 1972b; FROMMER et al. 1973; KRISHNAMURTHY et al. 1973) can be found. The results from the above works suggest that there are at least two states of water, one the free water and the other the bound water, captured in the membrane. Most of the NMR experiments, however, were conducted using wide-line proton magnetic resonance and few have been reported on the high resolution ^1H NMR spectra of water in the cellulose acetate mem-

brance. For example, Krishnamurthy and his coworkers (KRISHNAMURTHY et al. 1973) measured the high resolution ^1H NMR spectra of water in a wet ultrathin cellulose acetate membrane, which was rolled into the sample tube, without spinning and found that the resonance consisted of two very broad absorption curves of about 1200 Hz half-width. Yamabe and his coworkers reported also the existence of two water peaks in the high resolution ^1H NMR spectrum of cellulose acetate powder containing different quantities of water and assigned these peaks to the free and the bound water (YAMABE et al. 1972a; YAMABE 1972b).

In this work the high resolution ^1H NMR spectrum of water contained in several laboratory-made asymmetric membranes and in a dense membrane of cellulose acetate was obtained after immersing the membranes in water. Two sharp singlets were observed and they were assigned to the free and the bound water. The definitions of the terms "bound water" and "free water" in this paper are in order.

First the spaces in the membrane where water molecules are captured are conceived as pores, the wall of which is formed by cellulose acetate material. Then "bound water" is defined as water which is in the interfacial region of the pore wall and is under the strong influence of the interaction force from the pore wall. The term "free water" is defined, on the other hand, as water which is in the pore but is sufficiently apart from the pore wall. This water is not under the influence of the interaction force from the pore wall.

The ^1H spin-lattice relaxation time, T_1 , for these two singlets were also measured and the results were discussed in terms of the nature of the interaction forces working in water molecules and the properties of waters induced by such interaction forces.

Experimental

The asymmetric cellulose acetate membrane used in this study is the laboratory-made cellulose acetate 316 (10/30) membranes. The details of the membrane making methods are described in the earlier work, (PAGEAU, SOURIRAJAN 1972) using the following membrane casting conditions — casting solution composition: cellulose acetate (acetyl content = 39.8%) 17.0 wt-%, acetone 69.2 wt-%, magnesium perchlorate 1.45 wt-%, and water 12.35 wt-%, temperature of casting solution 10°C; temperature of casting atmosphere 30°C; humidity of casting atmosphere 55%, solvent evaporation time 1 min; gelation period in ice cold water >1h. The membranes thus produced were further shrunk in water at the temperature ranging from 60 ~ 82°C for ten minutes. A dense cellulose acetate membrane was produced by casting 20 wt-%

cellulose acetate (acetyl content = 39.8%) solution in acetone on a glass plate and evaporating the solvent at 104°C for 1h. The glass plate was then immersed into ice cold water and the membrane was removed.

For the preparation of an NMR sample, a membrane was wiped with a filter paper to remove extra external water. Then, it was rolled as a spiral into a 5 mm NMR sample tube and covered with water containing 10% deuterium oxide. The spectrum was obtained with spinning the tube on JEOL JNM-FX100 Fourier transform NMR spectrometer at 100 MHz. The signal of deuterium oxide was used for the field stabilization. The chemical shift was referred to water as an external standard. The proton spin-lattice relaxation time, T_1 , was measured by inversion-recovery Fourier transform method.

In the experiment below 27°C a membrane was rolled into a 3 mm polyethylene tube and covered with deuterium oxide. The polyethylene tube was then inserted coaxially into an ordinary 5 mm glass sample tube and the surrounding annulus was filled with chloroform- d_1 whose signal was used for field stabilization.

Results and Discussion

The ^1H NMR spectrum measured at 27°C for the asymmetric membrane shrunk at 82°C is shown in Figure 1A. The membrane was covered with water containing 10% deuterium oxide. Two water peaks were observed and they were about four Hz apart from each other. When increasing quantities of hydrochloric acid were added, these two peaks came to coalesce to a single sharp signal indicating the occurrence of a rapid proton exchange between two states of water (Figure 1B). However, the coalescence did not occur in the absence of acid even when the temperature was raised to 95°C although the broadening of the peaks occurred at higher temperature. The upfield small peak disappeared when the membrane was removed from the sample tube. The results indicate that the upfield peak can be assigned to the bound water, while the downfield peak corresponds to the free water in the membrane pore and the bulk water outside the membrane. The latter two kinds of water exchange rapidly with each other.

The peak of bound water molecules is separated from that of free and bulk water molecules even at a high temperature presumably due to the hydrogen bonding formed between the bound water molecule and the functional group on the cellulose acetate surface. Consequently, the probability of the hydrogen bonding with the surrounding water molecule is decreased and the upfield shift of the NMR peak is induced. On the other hand, $^1\text{H}-T_1$ of the bound water was shorter than that of the free water as shown in Table 1. This indicates

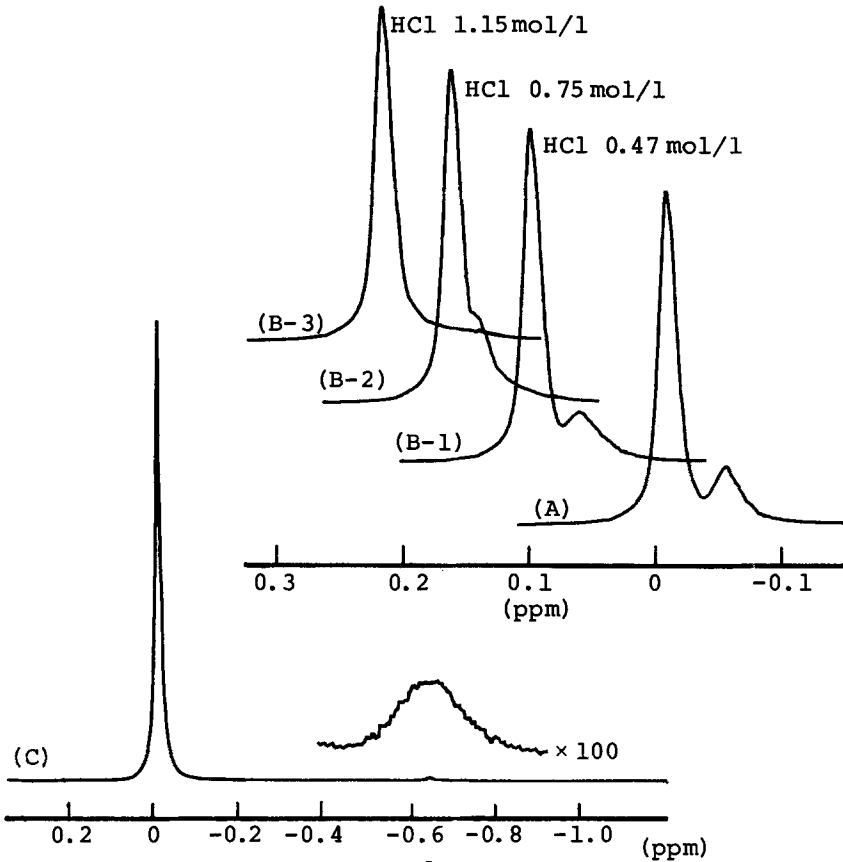


Figure 1. High resolution ^1H NMR spectra of water in cellulose acetate membranes. (A) Asymmetric membrane shrunk at 82°C ; (B) Same as A, in the presence of hydrochloric acid; (C) Dense membrane

Table 1. ^1H Chemical Shift and Spin-Lattice Relaxation Time, T_1 , of Water in Cellulose Acetate Membranes at 27°C ^a

Membrane	Shrinkage temperature ($^\circ\text{C}$)	$\Delta\nu^b$ (Hz)	T_1 (s)	
			Free	Bound
Asymmetric	60	4.0	3.4	2.1
Asymmetric	66	4.4	3.3	2.0
Asymmetric	72	4.5	3.3	2.0
Asymmetric	82	4.7	3.1	2.0
Dense	—	64.5	3.9	0.39

^a The asymmetric membrane (25 mm \times 40 mm) and the dense membrane (25 mm \times 60 mm) were rolled tightly into an NMR sample tube and covered with H_2O - D_2O mixture (D_2O 10 vol-%).

^b The difference between the chemical shifts of the free water and the bound water. The latter appears in the higher field than the former.

that the mobility of the bound water is less than that of the free and bulk water owing to the strong interaction with the cellulose acetate surface.

Furthermore, it was found that the $^1\text{H-T}_1$ of the bound water was very little affected by the shrinkage temperature of the membrane, as shown in Table 1, indicating that the shrinkage of the small pores in the active skin layer does not change the overall NMR spectrum, since the latter spectrum primarily represents the state of water in the sublayer of large pore sizes of asymmetric membranes.

As shown in Figure 2, these two peaks broadened with a decrease in temperature, and at 0°C the signal due to the free water disappeared, while that due to the bound water remained even at -15°C . Frommer et al (1973) reported that NMR free induction decay signal of water in cellulose acetate membranes observed at $0 \sim -60^\circ\text{C}$ consisted of a fast decaying component ($T_2 \approx 30 \sim 50\mu\text{s}$) and a slow-decaying component ($T_2 \geq 1\text{ ms}$), which were assigned to the freezing and the nonfreezing water, respectively. In our experiment using the high resolution NMR technique the signals due to these two components were observed as separate peaks and the bound water was directly evidenced to be nonfreezing.

Although there is no justification, the dense membrane has often been used to simulate the active skin layer of the asymmetric porous cellulose acetate membrane. In this work the NMR spectrum of the dense cellulose acetate membrane was studied in order to compare with that of the asymmetric cellulose acetate membrane. The NMR spectrum exhibited also two water peaks as shown in Figure 1C. However, the peak due to the bound water in the dense membrane appeared at a much higher magnetic field and its intensity was much weaker as compared with that observed for the asymmetric membrane. The $^1\text{H-T}_1$ of the bound water in the dense membrane was shorter and the line width of the signal was broader than those for the asymmetric cellulose acetate membrane. These results indicate that the bound water in the dense membrane is more strongly associated with the cellulose acetate surface than in the asymmetric membrane.

In this work the existence of the bound water in cellulose acetate membranes was confirmed. The bound water at the polymer-water interface is more strongly associated with the polymer surface than the surrounding water molecules, and therefore the property of the bound water is under the influence of the polymer material. When the interface is formed between the membrane polymer and the solution, the solute distribution takes place between the bound and the free water. In some cases the solutes such as electrolytes are less distri-

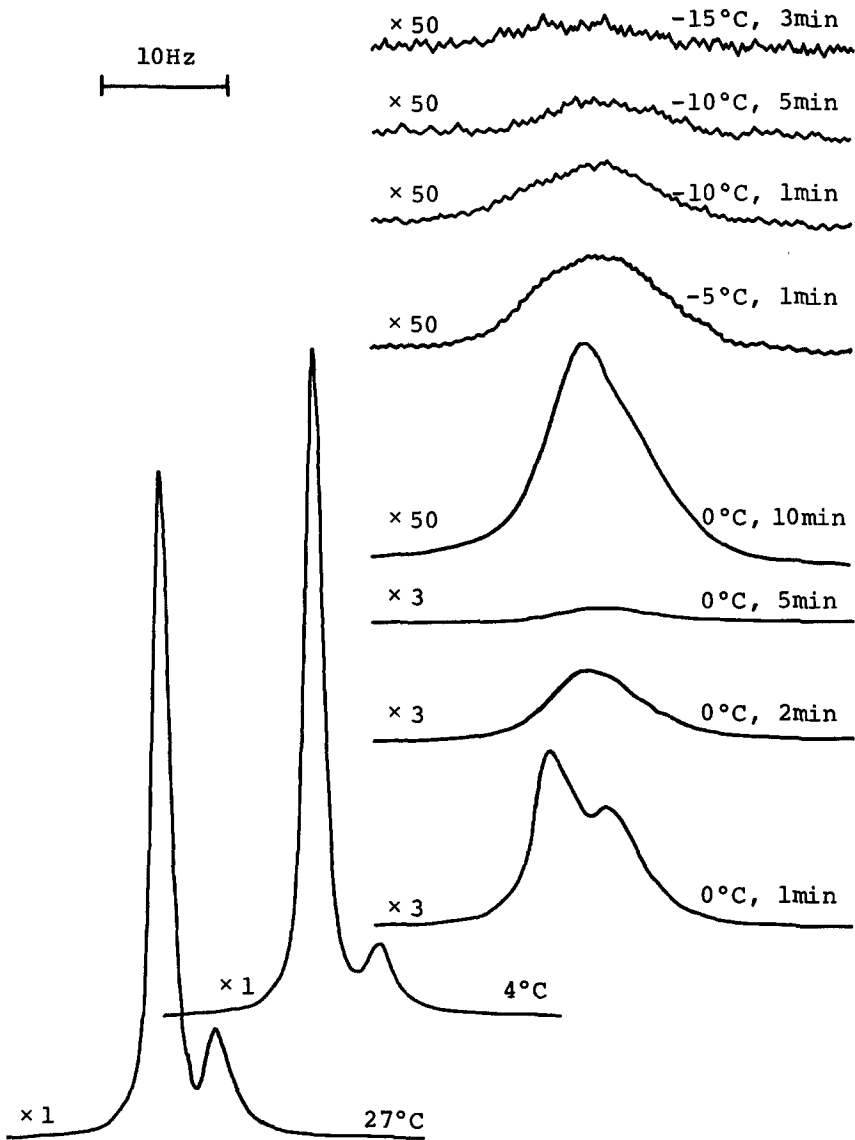


Figure 2. Temperature dependence of ^1H NMR spectra of water in an asymmetric membrane

buted in the bound water due to the weaker solvation ability of the latter water to the ions, while in other cases solutes are more distributed in the bound water due to the stronger attractive force working between the membrane material and the solute. The concentration gradient of the solute at the interfacial region thus produced should naturally be one of the factors governing solute transport and hence the performance of the reverse osmosis membrane.

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