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## Liquid Membranes at the Cellulose Acetate Membrane/Saline Solution Interface in Reverse Osmosis. II. Spectrophotometric Evidence for Surfactant—Water Interactions

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### INTRODUCTION

In an earlier study [1], a surfactant layer at the interface between a cellulose acetate membrane and a saline solution in reverse osmosis was shown to act as a liquid membrane in series with the solid membrane gel. Inasmuch as the effectiveness of liquid membranes in increasing the permselectivity of the underlying gelatinous membranes increased with increasing surfactant hydrophilicity, it was postulated that solute rejection was at least partially attributable to the water-binding capacity of the various surfactants. In the present study, spectrophotometric evidence for the existence of surfactant-water interactions is presented.

### EXPERIMENTAL

Poly(vinyl methyl) ether, PVME (Gantrez M-154, General Aniline and Film), a polyoxyethylenenonyl phenol containing nine moles of ethylene oxide per mole of nonylphenol (Dowfax 9N-9, Dow Chemical); a polyoxyethylene-polyoxypropylene block copolymer (Pluronic L-64, Wyandotte Chemical); and sodium dodecyl sulfate were exhaustively dried in vacuo. Aqueous solutions containing 50% by weight were prepared of all but the sodium dodecyl sulfate, for which a saturated solution was employed. The spectra of both the pure surfactants and their aqueous solutions were obtained on a Perkin-Elmer Model 21 spectrophotometer utilizing cells containing Irtran windows.

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## EXPERIMENTAL RESULTS

### Poly(vinyl methyl) ether

A 0.15- $\mu$  shift to longer wavelengths of the C—O—C asymmetric stretching band (9.25  $\mu$ ) occurs in the presence of water (Fig. 1). Such a shift is indicative of hydrogen bonding between water and the ethereal oxygens. A similar shift occurred in the —O—CH<sub>3</sub> asymmetric and symmetric deformation bands, which also occur at 6-8  $\mu$ .

### Polyoxyethylenonylphenols

A shift of 0.2  $\mu$  to longer wavelengths is apparent in the C—O—C asymmetric stretching band ( $\sim 9$   $\mu$ ) of the polyoxyethylenonylphenol in the presence of water (Fig. 2). However, no shift was noted in the asymmetric band at 8  $\mu$  associated with the  $\phi$ -O group. These results indicate extensive hydrogen between water and the aliphatic ether groups but no bonding to the aromatic ether groups. Lack of bonding to the latter can be attributed to steric hindrance and/or the hydrophobicity of the aromatic ring.

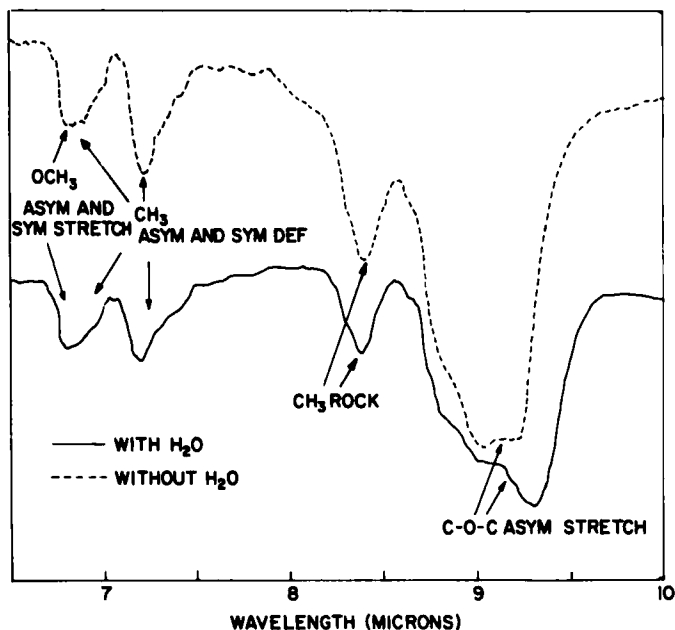


Fig. 1. Infrared spectra of poly(vinyl methyl) ether in the presence and absence of water.

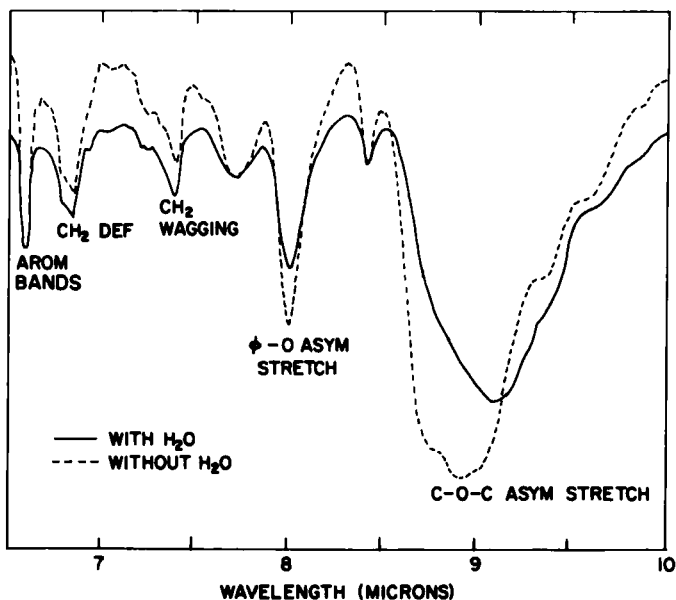


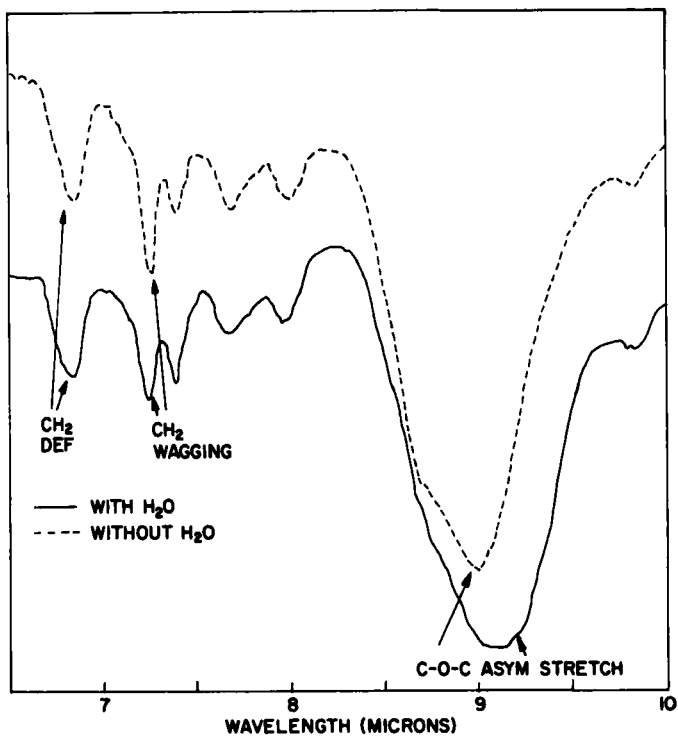
Fig. 2. Infrared spectra of polyoxyethylenenonylphenol in the presence and absence of water.

### Polyoxyethylene-Polyoxypropylene Block Copolymers

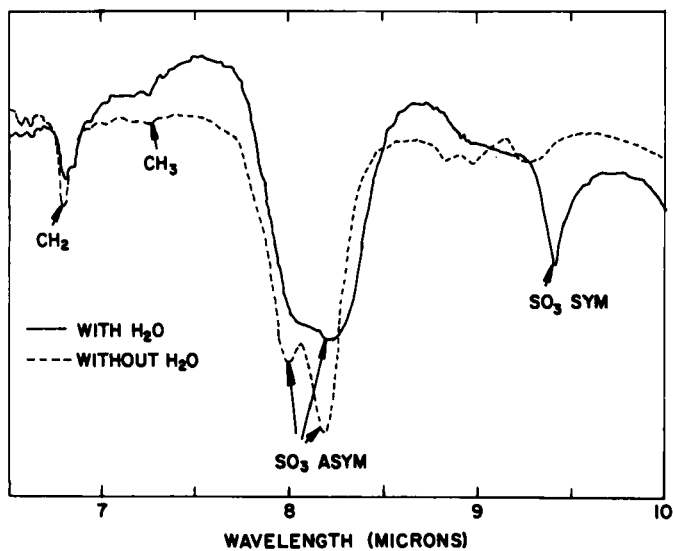
In this particular surfactant (Pluoronic L-64), the typical molecular weight of the hydrophobic polyoxypropylene portion is 1750, and that of the hydrophilic polyoxyethylene portion, 1150. A shift of  $0.1 \mu$  toward longer wavelengths was noted in the C—O—C asymmetric stretching band at  $9 \mu$ , indicating a slight amount of hydrogen bonding of water to the ethereal oxygens (Fig. 3). Because of the hydrophobic nature of the polyoxypropylene block, this bonding is probably to the oxygens of the polyoxyethylene portions of the polymer.

### Sodium Dodecyl Sulfate

Although changes in the shape of the band for the asymmetric  $\text{SO}_3$  group occurred when water was removed, it is likely that these changes are due primarily to the liquid (solution) to solid phase change which also occurs (Fig. 4). No significant hydrogen bonding is indicated.



**Fig. 3.** Infrared spectra of a polyoxyethylene-polyoxypropylene block copolymer in the presence and absence of water.



**Fig. 4.** Infrared spectra of sodium dodecyl sulfate in the presence and absence of water.

## DISCUSSION

Materials which are known to function as feed additives, e.g., poly(vinyl methyl) ether and the polyoxyethylene nonylphenols, show extensive hydrogen bonding of water to the closely spaced aliphatic ethereal oxygens. Sodium dodecyl sulfate, which does not increase the permselectivity of the underlying gelatinous membrane, does not show such an association with water. Pluronic L-64 is also ineffective as a feed additive although it does show some tendency to associate with water (albeit a lesser tendency than is observed with the effective feed additives).

This lesser tendency to bind water is due to the dilution of the hydrophilic polyoxyethylene with hydrophobic polyoxypropylene blocks. The fact that a complete absence, rather than a mere diminution, of the feed additive effect is observed is probably attributable to the substantial size of the hydrophobic blocks separating bound water domains.

Thus it appears probable that the formation of hydrogen bonds between water and the surfactant is a necessary but not sufficient requisite to the effectiveness of the surfactant as a feed additive. Uniformly distributed, closely spaced regions of strongly bonded water, as in the cases of PVME and the polyoxyethylenenonylphenols, must be present if an effective barrier to salt transport is to result. If nonbonded water, as in the case of sodium dodecyl sulfate, or water bonded to blocks that are widely separated by blocks that do not bind water, is present, the resultant liquid membranes are ineffective barriers. It may be inferred, therefore, that the permselectivity of liquid membranes, as does that of their solid counterparts, depends not only upon their chemical structure affecting absolute water binding capacity, but also upon their physical structure affecting continuity between bound water domains and uniformity in inter-chain displacement of their component macromolecules.

## ACKNOWLEDGMENT

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