STABILIZATION OF CELLULOSIC DESALINATION MEMBRANES
BY CROSSLINKING

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INTRODUCTION

C. E. Reid and coworkers[1] discovered that, among many polymers, cellulose acetate exhibits an exceptionally selective permeability toward water in salt solutions under conditions of reverse osmosis. Subsequently, Loeb and Sourirajan[2] developed a method of fabrication for water-swollen cellulose acetate membranes with greatly increased flux rates but which retain much of the selectivity ("salt rejection") of ordinary films. The practicality of the so-called asymmetric membranes of this type is now established by their use in commercial reverse osmosis desalination equipment. Further increases in water flux, however, are highly desirable in order to reduce the cost of the reverse osmosis process. The preparation of membranes with both increased flux and improved flux stability was the object of the work described herein.

Figure 1 shows the asymmetric structure of a cellulose acetate membrane in cross section. This microphotograph, taken with a scanning electron microscope, shows an extremely thin layer (in the upper part of the photograph) surmounting a relatively thick (50 to 100 μm) substructure with pores about 0.3 μm in diameter. The high flux rates of water in reverse osmosis result from the thinness of the top layer (ca. 0.05 μm) and the selectivity depends on the absence of pores in this thin "active layer." Water (and salt) permeate freely through the supporting porous substructure.
Water is believed to permeate the active layer by a pressure-driven solution-diffusion mechanism while hydrated solute ions are relatively efficiently excluded by their large size and low solubility in cellulose acetate. More highly charged ions are more efficiently rejected than those of lower charge (e.g., $\text{SO}_4^{2-} > \text{Cl}^-, \text{Ca}^{++} > \text{Na}^+$) [3,4]. The overall permeabilities of both water and ions are believed to be controlled by the amount of water dissolved in the active layer of the cellulose acetate (cellulose acetate sorbs about 12% by weight of water at 100% relative humidity). For example, Yasuda et al. have shown that for both salt and water $\log D = \log D_0 - K[(1/H) - 1]$, where $D$ is the diffusion coefficient in the polymer, $D_0$ is the diffusion coefficient in