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PREPARATION OF ASYMMETRIC LOEB-SOURIRAJAN MEMBRANES

Introduction

In recent years the technique of preparation of "skin type" asymmetric cellulose acetate membranes first developed by Loeb and Sourirajan (1) has been applied successfully to other polymers. Today a significant number of "skin type" noncellulosic membranes are described in the literature (2,3). However, the preparation of Loeb-Sourirajan membranes remains an empirical procedure, and only recently have more systematic approaches been used to rationalize the variables of the preparation procedure (4–7). These studies have shown that in addition to the polymer used as the membrane material, the solvent in the casting solution has a critical influence on the transport properties of the resulting membranes. In this study, the effect of the solvent in the casting solution, and of its rate of exchange with nonsolvent, on the overall porosity of membranes prepared from various polymers was investigated.

Experimental Procedures and Results

A casting solution containing 15% by weight of a given polymer in the appropriate reagent-grade solvent was prepared. The polymer was used as supplied by the manufacturer without further purification. A 10 mil thick wet film was cast from this solution onto a glass plate with a Gardner draw-down bar. The cast film was immediately immersed in a water bath (ca. 20°C) to precipitate the membrane, which was then leached overnight in running water to remove the last traces of solvent.

The overall porosity of a membrane was determined by measuring its water content after the final leaching procedure. A membrane sample of ca. 0.1-0.2 g equilibrated in the water bath was quickly blotted by a paper towel to remove surface water and weighed. The membrane sample was then dried in a vacuum oven at 60°-70°C and weighed again. Water contents determined by the weight difference of the wet and dry samples were reproducible within ±2%.

The experimental results are summarized in Table I, which shows the water content of membranes made from different polymers and solvents. The solvents are listed in order of their solubility parameters, which were obtained from the literature (8,9). Because of the particular importance of cellulose acetate membranes, the data for this polymer are plotted in Figure 1, including a few additional solvents used in this case.

The results of this study show strikingly that the water content of nearly all membranes increases with increasing solubility parameter, independently of the nature of the polymer. Tetrahydrofuran always gives very dense membranes and

TABLE I

Water Content, in Percent by Weight of Swollen Membrane, and Fluxes through Cellulose Acetate Membranes as Function of Solubility Parameter.

		Polymer								
Solvent	Solvent Solubility Parameter	Cellulose Acetate (Eastman E398-3)	Polystyrene (Dow 1683)	Poly(vinyl chloride) (Hooker Chem. Co. PVC-B-34)	Poly(vinylidine fluoride)(Pensalt Kynar 201)	Polycarbonate (GE Lexan 105)	Polyethylmethyacrylate (Dupont Lucite 2042)	Polyacrylonitrile (Dupont PAN "A")	Polyacrylonitrile Poly(vinyl chloride) copolymer (Union Carbide Dynell)	Relative fluxes of solvent/ water across a cellulose acetate membrane (Ref. 6)
Tetrahydrofuran	9.1	33	insol.	11	insol.	9	insol.	insol.	insol.	–
Propylene oxide	9.2	15	–	–	–	–	–	–	–	–
Ethyl formate	9.4	18	–	–	–	–	–	–	–	–
Acetone	9.9	47	insol.	insol.	insol.	insol.	40	insol.	insol.	very large
Ethyl lactate	10.0	73	–	–	–	–	–	–	–	–
Dioxane	10.0	82	58			30	70			2.3
Acetic acid	10.1	83	insol.	insol.	insol.	insol.	73	insol.	insol.	2.2
Dimethylacetamide	10.8	85	74	68	55	insol.	77	insol.	77	–
Triethylphosphate	10.9	85	81	insol.	72	insol.	69	insol.	insol.	1.0
N-Methyl pyrrolidone	11.3	87	82	78	77	77	80	80	80	–
Dimethylsulfoxide	12.0	87	insol.	insol.	80	insol.	insol.	79	insol.	0.6
Dimethylformamide	12.1	84	72	58	52	insol.	insol.	81	77	0.5

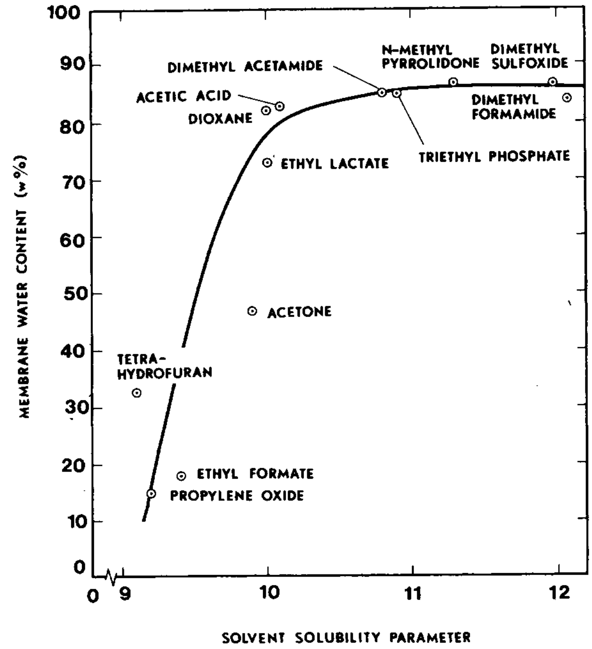

Fig. 1

dimethylsulfoxide always gives very porous membranes. If mixtures of solvents are used, the same general relation is observed, even when one of the components is by itself not a solvent for the particular polymer. Of the 41 polymer-solvent systems investigated, in only 7 cases was the water content out of line with the solvent solubility parameter, within the limits of error of the experiments, and of the 7 exceptions, 5 were dimethylformanide casting solutions, which consistently gave membranes of lower porosity than the solubility parameter would suggest.

The results of Table I are even more remarkable considering the range of solubility parameters of the polymers–from 14.0 for the most polar polymer (polyacrylonitrile) to 8.9 and 7.5, respectively, for the relatively nonpolar and hydrophobic polymers (polystyrene and poly(vinyl idine fluoride)).

Discussion

Recently, Frommer et al. (6) have measured the transport of solvent and water across a swollen, porous cellulose acetate membrane, held in a permeability cell to separate water from a solution of 40% solvent in water. The fluxes measured in these experiments partially correspond to the situation during the formation of a membrane in the Loeb-Sourirajan process where water diffuses into the polymer casting solution and solvent diffuses out. The ratios of the rates of exchange (fluxes), of solvent and water measured by Frommer et al.

(6) are listed in the last column of Table I. The porosity of the final membrane correlates well with this flux ratio, though these fluxes were measured in an already formed membrane. Frommer's results taken together with ours indicate that the membrane porosity may be largely governed by the rate of diffusive exchange of solvent and water during the precipitation of the polymer. Thus, when water diffuses into the solution film much faster than solvent leaves, rapid fibrous precipitation occurs and a porous membrane is formed. Conversely, if solvent leaves faster than water enters, the polymer desolvates more orderly and a dense, collapsed, membrane is formed. In general, water will enter the solution layer the faster, the closer the solvent solubility parameter approaches its own.

One explanation for these results might be that polymers dissolved in solvents of high solubility parameter remain in solution even in the presence of appreciable quantities of imbibed water, leading to porous membranes, while solutions made from solvents of low solubility parameter are less able to tolerate imbibed water and soon precipitate, leading to dense membranes. Unfortunately, the evidence does not support this simple explanation. In the case of cellulose acetate, for example, a 20% polymer solution in DMSO ($\delta = 12.0$) precipitates after imbibing only 14% water by weight, considerably less water than a 20% polymer solution in acetone ($\delta = 9.9$), which precipitates after imbibing 28% water (6).

Our own electron microscopic observations, surface dyeing studies, and the leveling off of the curve in Figure 1 suggest that additional factors determine, or modify, this correlation among membrane water content ("porosity"), fluxes, and solubility parameters. We believe that the most important of these is a thin film of polymer (skin) that forms almost immediately on contact between water and a solution of a water-insoluble polymer. From solvents of low solubility parameter, this polymer film plus residual solvent constitutes an effective barrier against water, but not against the solvent, i.e., it is largely semipermeable. Since our solvents are all highly, or infinitely, miscible with water, they move out rapidly, leaving a collapsed polymer film behind. As the value of δ rises, the water content of the initial skin rises too and renders it less permeable to the solvent and more to the water. Eventually, the flux becomes preponderantly one of water into the polymer solution. If this happens, the polymer beyond the skin precipitates in a dendritic, cavernous, form rigid enough to act as a sponge, i.e., retain water by capillarity even after the solvent has eventually diffused out. Some tests on this supposition are under way, especially with a view to ascertaining whether the primary film asymmetry is due to oriented structures. One with the more polar groups on the polymer in the center of the film would be water repellant, the other with the polarizable or polar groups on the outside, would be water permeable. Such polarized sheet membrane structures could be expected in view of the frequently found (2) corresponding organization of the individual coacervate droplets before their coalescence and precipitation,

The correlations of Table I and Figure 1 are extremely useful results for the practicing membrane technologist. Until now, membrane casting solutions frequently contained four or five or even more components and recipes were usually arrived at after an extensive trial and error development. Table I should considerably speed this type of development and holds useful clues in the search for a rational basis at arriving at Loeb-Sourirajan casting solutions.

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