

# Integrally Skinned Polysulfone Hollow Fiber Membranes for Pervaporation

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## SYNOPSIS

From polysulfone as polymer, integrally skinned hollow fiber membranes with a defect-free top layer have been spun. The spinning process described here differs from the traditional dry-wet spinning process where the fiber enters the coagulation bath after passing a certain air gap. In the present process, a specially designed tripple orifice spinneret has been used that allows spinning without contact with the air. This spinneret makes it possible to use two different nonsolvents subsequently. During the contact time with the first nonsolvent, the polymer concentration in the top layer is enhanced, after which the second coagulation bath causes further phase separation and solidification of the ultimate hollow fiber membrane. Top layers of  $\pm 1 \mu\text{m}$  have been obtained, supported by a porous sublayer. The effect of spinning parameters that might influence the membrane structure and, therefore, the membrane properties, are studied by scanning electron microscopy and pervaporation experiments, using a mixture of 80 wt % acetic acid and 20 wt % water at a temperature of 70°C. Higher fluxes as a result of a lower resistance in the substructure could be obtained by adding glycerol to the spinning dope, by decreasing the polymer concentration, and by adding a certain amount of solvent to the bore liquid. Other parameters studied are the type of the solvent in the spinning dope and the type of the first nonsolvent.

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## INTRODUCTION

Polysulfone (PSF) is a highly chemical resistant polymer and has a preferential permeability for water in the pervaporation process. This makes the polymer interesting as a membrane material for the dehydration of organic acids, where chemical resistance of the membrane material is a necessary requirement.

PSF is also an excellent material for the preparation of hollow fiber membranes, which have a favorable surface area : volume ratio compared to flat membranes; this is the reason why PSF also has been widely studied as a material for the spinning of hollow fiber membranes, for all kinds of separation purposes.

Cabasso et al. used polyvinylpyrrolidone (PVP) as an additive to the PSF spinning dope and investigated mechanical and transport properties of porous hollow fibers as a function of the bore liquid composition and the spinning dope viscosity<sup>1</sup> as well as the membrane morphology.<sup>2</sup>

Kuraray Co., Ltd.<sup>3</sup> has patented a spinning process to prepare porous PSF hollow fiber membranes that can be used for water purification and blood filtration. In the spinning dope, polyethylene glycol was used as an additive.

Henis and Tripodi<sup>4,5</sup> described a method on how to prepare highly permselective and effectively high flux gas separation membranes from porous PSF hollow fiber membranes using a postcoating procedure with an appropriately chosen material (e.g., polydimethylsiloxane) in order to plug the pores. In this way, the intrinsic selectivity of the support material could be obtained.

Fritzsche and Kesting et al.<sup>6-13</sup> published extensively about the spinning process and the structure of PSF hollow fiber membranes for gas separation

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and applied the same coating procedure as Henis and Tripodi did<sup>4,5</sup> to obtain the required gas separation properties. By using Lewis acid : base solvent complexes, the permeability of the first generation membranes<sup>4</sup> was increased substantially.

Pervaporation membranes act in principle the same as gas separation membranes; they both need a dense, nonporous layer to separate the components by a difference in solubility, and diffusivity. In order to obtain a flux as high as possible, this layer should be very thin. Homogeneous films thinner than 3–5  $\mu\text{m}$  can be made, but are very hard to handle due to loss of mechanical strength.

The development of asymmetric membranes by Loeb and Sourirajan<sup>14</sup> in the early sixties offered new perspectives for the development of high flux membranes. Nowadays, almost all commercially produced ultrafiltration, microfiltration, and hyperfiltration membranes are asymmetric and completely or partially prepared by the phase inversion process.

For high-flux pervaporation and gas separation membranes the phase inversion process is also used for preparing the porous sublayer, which serves as a support for a highly selective ultrathin homogeneous layer applied in a second step. The homogeneous dense top layer is responsible for the selective separation, while the transport resistance of the support has to be negligible.

If the support by itself has a low surface porosity with a small pore size, the support can also be coated with a highly permeable material, i.e., polydimethylsiloxane, in order to plug the pores. In this case, the separation will be determined by the asymmetric support layer itself, as was applied by Henis and Tripodi<sup>4,5</sup> and Fritzsche et al.<sup>6,7</sup> A disadvantage of the preparation of these membranes is an extra coating step that is required to get the ultimate membrane properties.

A one-step method to produce integrally skinned asymmetric membranes with an ultrathin top layer has been studied by Pinnau et al.<sup>15,16</sup> In this dry-wet phase inversion process a combination of two solvents and one or two nonsolvents is used, with one of the solvents being highly volatile. After casting the polymer solution on an impermeable support, a water-saturated air stream is blown over the membrane surface for about 10 s, followed by another 10 s of free evaporation before the nascent membrane is coagulated. So far, only flat membranes could be made according to this procedure, resulting in membranes with top layers of 300–1000 Å. If one would apply this procedure for the spinning of hollow fi-

bers, this would mean an air gap of about 1 meter at a spinning rate of 3 m/min, which is impossible.

Another type of one-step method was developed by Mulder et al.<sup>17</sup> They used two solvents, a volatile "poor" solvent and a nonvolatile "good" solvent. The only preparation parameter in this "evaporation-induced delayed demixing" method is the evaporation time. Also, by this method, defect-free top layers have been prepared with a thickness < 1000 Å.

A different preparation process for gas separation membranes was developed by van't Hof et al.<sup>18,19</sup> This so-called "dual bath spinning" procedure, where the membrane is brought into contact with two different nonsolvents consecutively, can be used successfully to prepare hollow fiber membranes. A small adjustment of the commonly used tube-in-orifice spinneret made this process extremely easy to handle.<sup>20,21</sup> An additional orifice in the spinneret (Fig. 2) offers the possibility to introduce a certain nonsolvent as a first coagulant, together with the polymer spinning dope via the spinneret into a coagulation bath filled with a second nonsolvent. By varying the distance between the spinneret and the second nonsolvent bath, the possibility is offered to vary the contact time with this first coagulant. During this contact time the polymer concentration in the top layer is increased, which results in a dense top layer after solidification by liquid-liquid demixing upon immersion in the second nonsolvent. The influence of different spinning parameters, like the polymer concentration, the additive concentration in the polymer spinning dope, the type of solvent for the polymer, the type of nonsolvent used as a first coagulant, and the composition of the bore liquid were investigated. The hollow fiber membranes were tested for the dehydration of 80 wt % acetic acid in water at 70°C in a pervaporation setup. The choice of this composition and temperature was based on targets specified in a BRITE-project where this work was part of.

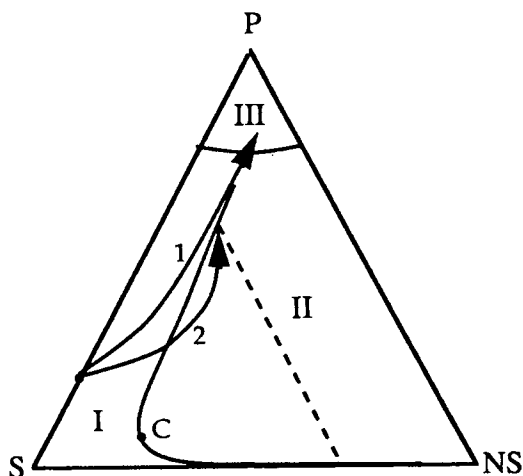
## THEORY

Delayed demixing is a process in which it takes a certain period of time between the moment of immersion of the polymer solution in the nonsolvent bath and the onset of phase separation. This interval is caused by the difference in velocity of inflow of nonsolvent into the polymer solution and outflow of solvent from the polymer solution into the nonsolvent bath.<sup>22</sup> The relatively large outflow of solvent compared to the small inflow of nonsolvent results

in an increase of the polymer concentration, especially at the interface polymer solution/coagulation bath. By the time liquid-liquid demixing starts, the polymer concentration at the interface has become so large that the vitrification boundary is crossed (Fig. 1, path 1) and a thin, dense top layer is formed after solidification. During the interval of immersion and onset of phase separation, not only the polymer concentration of the top layer increases, but also, to a smaller extent, the polymer concentration in the sublayer. This goes on until the top layer becomes so dense that it will hinder the outflow of solvent from just behind this layer, resulting in liquid-liquid demixing of the sublayer at lower polymer and higher nonsolvent concentrations compared to the top layer (Fig. 1, path 2). Starting with a polymer concentration normally used in membrane preparation, the demixing gap will be passed above the critical point at the polymer-rich side. This means that nucleation and growth of the polymer lean phase takes place, resulting in a porous structure.

Because of the increase in the polymer concentration in the beginning of the process of membrane formation, the chance that the porous sublayer may consist of a closed cell structure will also increase; the higher the polymer concentration, the thicker the ultimate wall between the pores.

Delayed demixing typically occurs when the interaction of the solvent and the nonsolvent is rather poor, i.e., for the combination of *N*-Methylpyrrolidone (NMP), *N,N*-Dimethylacetamide (DMAc),



**Figure 1** Schematic representation of the precipitation process. I. Homogeneous polymer solution; II. Liquid-liquid demixing region; III. Gel or vitrification area; C is critical point; 1, possible composition path of the toplayer; 2, possible composition path of the sublayer.

*N,N*-Dimethylformamide (DMF), or Formylpyrrolidone (FP) as solvent and glycerol, iso-propanol, butanol, or pentanol as nonsolvent. All these solvent-nonsolvent pairs show a large excess free enthalpy of mixing.

Instantaneous demixing is a process in which liquid-liquid demixing immediately occurs upon immersion of the polymer solution in the nonsolvent bath. The difference in the velocity of outflow of solvent from the polymer solution and inflow of nonsolvent into the polymer solution is not so large anymore. Because of the rapid solidification, a thin interfacial layer of relative high polymer concentration is formed. Only when highly concentrated polymer solutions are used pore-free top layers may be obtained, but in this case, the overall resistance of the membrane is very high. In the sublayer, the polymer concentration will hardly have changed, nucleation and growth of the polymer lean phase results in a relatively open and porous substructure. Very often macrovoids can be seen to occur. They have the appearance of large, outgrown nuclei, starting directly below the top layer and sometimes extending over the major part of the thickness of the membrane. Their origin stems from the lack of formation of new nuclei once a layer of nuclei has been formed. In recent theoretical work<sup>22,23</sup> this has been explained as the turnover to conditions of delayed demixing in front of formed nuclei, originating from the altered ratio of diffusive flows of solvent and nonsolvent to and from the coagulation bath, respectively, to and from the already formed nuclei.

Instantaneous demixing typically occurs when solvent and nonsolvent show good interaction, like between NMP, DMAc, DMF, or FP as solvent and water as nonsolvent.

In the dry-wet spinning process the membrane is normally formed by phase inversion precipitation of the extruded polymer solution from two sides, viz. by a coagulation bath at the outside, possibly after passage through an air gap and by a bore coagulant at the inside.

An ideal membrane for pervaporation is a membrane with a very thin defect-free top layer supported by an open, porous sublayer having negligible transport resistance. A membrane that obeys these properties cannot be obtained by one of the above-described demixing processes separately. A combination of the two processes using two different nonsolvents as a coagulant at the outside, the first one causing delayed demixing followed by a second nonsolvent causing instantaneous demixing, has been shown to be a good approach.<sup>18,19</sup>

An extra orifice in the spinneret makes it possible for the extruded polymer dope to get into direct contact with the first nonsolvent immediately after it leaves the spinneret. The contact time with the first nonsolvent bath is very critical. The top layer should be thin and defect-free, and the polymer concentration in the sublayer may not be increased too high in order to achieve an open, porous substructure. In other words, an optimum contact time should be found to produce a defect-free top layer and short enough to obtain a top layer as thin as possible. As soon as the nascent fiber enters the second nonsolvent the first nonsolvent will be exchanged by the second nonsolvent, resulting in instantaneous demixing conditions and the top layer is fixed.

In order to achieve a porous low-resistant sublayer, additives (e.g., nonsolvents) can be added to the spinning dope, (a) to make the polymer solution more sensitive to nonsolvent inflow or (b) to obtain a composition of the polymer solution close to the binodal composition; this results in a deeper penetration of the demixing gap.

For hollow fiber membranes with the separating layer at the outside as a bore liquid, a nonsolvent of the second type, causing instantaneous demixing, or a mixture of nonsolvent and solvent, which may give some delayed demixing dependent on the solvent content, are preferred.

## EXPERIMENTAL

### Materials

Polysulfone (PSF, Udel P 3500) was obtained from Amoco, silicon rubber (RTV 106, General Electric) was obtained from Benecom BV, glycerol (anhydrous extra pure), iso-propanol (i-PrOH), pentanol, *N*-methylpyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc), and formylpiperidine (FP) were obtained from Merck. The solvents were of analytical grade and used without further purification.

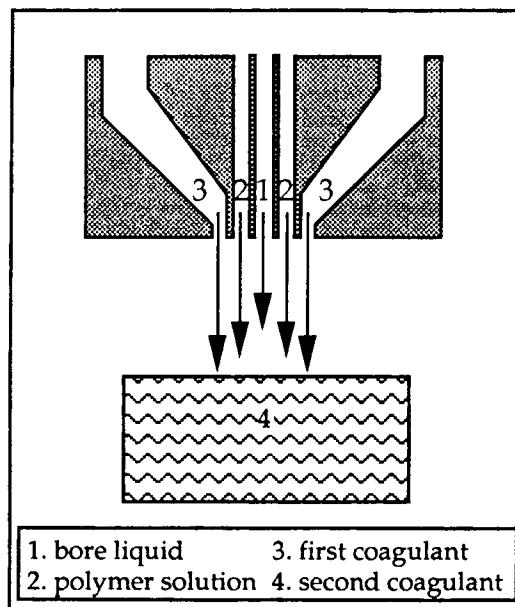
### Fiber Spinning

Predried polysulfone (at least for 1 week in a vacuum oven at 150°C) was dissolved in NMP at various concentrations, without and with glycerol as an additive. Also, DMAc and FP were used as solvents for PSF. The polymer solutions were filtered and degassed before spinning. To control the contact time with the first nonsolvent and to be able to use all kinds of nonsolvents that result in delayed demixing, a spinneret has been developed in the re-

search group at the University of Twente with a tube and two orifices<sup>20,21</sup> (Fig. 2); the tube for the bore liquid (1), one orifice for the polymer solution (2), and one orifice for the first nonsolvent (3). As a bore liquid, water and water/NMP mixtures were used. The first nonsolvent, the second nonsolvent, and the bore liquid had a temperature of 22–24°C. After immersion in the second nonsolvent bath, the fibers were placed into a hot water bath and cut into lengths of 40–50 cm and rinsed in hot water for at least 24 h. Subsequently, the fibers were immersed in an ethanol bath for at least 5 h followed by immersion in a hexane bath for another 5 h. At last the fibers were dried in air at room temperature. The spinning speed varied from 3.5 to 5 m/min.

### Delayed Demixing

Delay times of demixing could be measured by a simple light transmission technique as described by Reuvers et al.<sup>22</sup> and van't Hof et al.<sup>18</sup> The polymer solution is cast on a glass plate with a 0.5 mm casting thickness and immediately immersed in the nonsolvent. A desk lamp is put over the nonsolvent bath and acts as the light source. At the bottom side of the nonsolvent bath a detector measures the light transmittance as a function of time. Due to optical inhomogeneities caused by phase separation, the light transmittance starts to decrease. An immediate reduction of the light transmittance is characteristic



**Figure 2** Schematic representation of the triple orifice spinneret.

for nonsolvents that cause instantaneous demixing, and a certain delay time before reduction of the light transmittance takes place can be observed for other nonsolvents. Several nonsolvents were investigated for their delay times of demixing to see whether they are suitable to serve as a first coagulant.

### Pervaporation

The hollow fiber membranes were tested for pervaporation using a feed mixture of 80 wt % acetic acid and 20 wt % water at a temperature of 70°C. Therefore, modules were made consisting of two fibers at a length of approximately 15 cm. A one-component silicon rubber (RTV 106) was used as potting material. The permeate side was maintained at a pressure of 0.1–0.2 mmHg by an Edwards two-stage vacuum pump. The pressure was measured by an Edwards pirani meter. Permeate samples were taken every hour for 8 h. Steady state was normally obtained after 2–3 h. The permeate was analyzed using a Varian 3700 Gas Chromatograph filled with a Poropak Q column at a temperature of 190°C. A schematic representation of the pervaporation setup is given in Fig. 3.

### Scanning Electron Microscopy

Samples for scanning electron microscopy (SEM) were made by cryogenic breaking of the fibers after being soaked in a water/ethanol mixture. The broken samples were dried under vacuum and coated with a thin gold layer by means of sputtering. A JEOL JSM-T 220A Scanning Microscope was used.

## RESULTS AND DISCUSSION

### First Coagulation Bath

Several nonsolvents have been studied with respect to their ability to be used as a first coagulant in the spinning process of PSF hollow fiber membranes for pervaporation. The first nonsolvent must show delayed demixing, which is the first step to obtain a dense and defect-free top layer responsible for the separation. The longer it takes before liquid–liquid demixing occurs after immersion of the polymer solution in the nonsolvent, the larger the ratio outflow of solvent and inflow of nonsolvent layer will be, and the denser and thicker the interfacial layer will become.

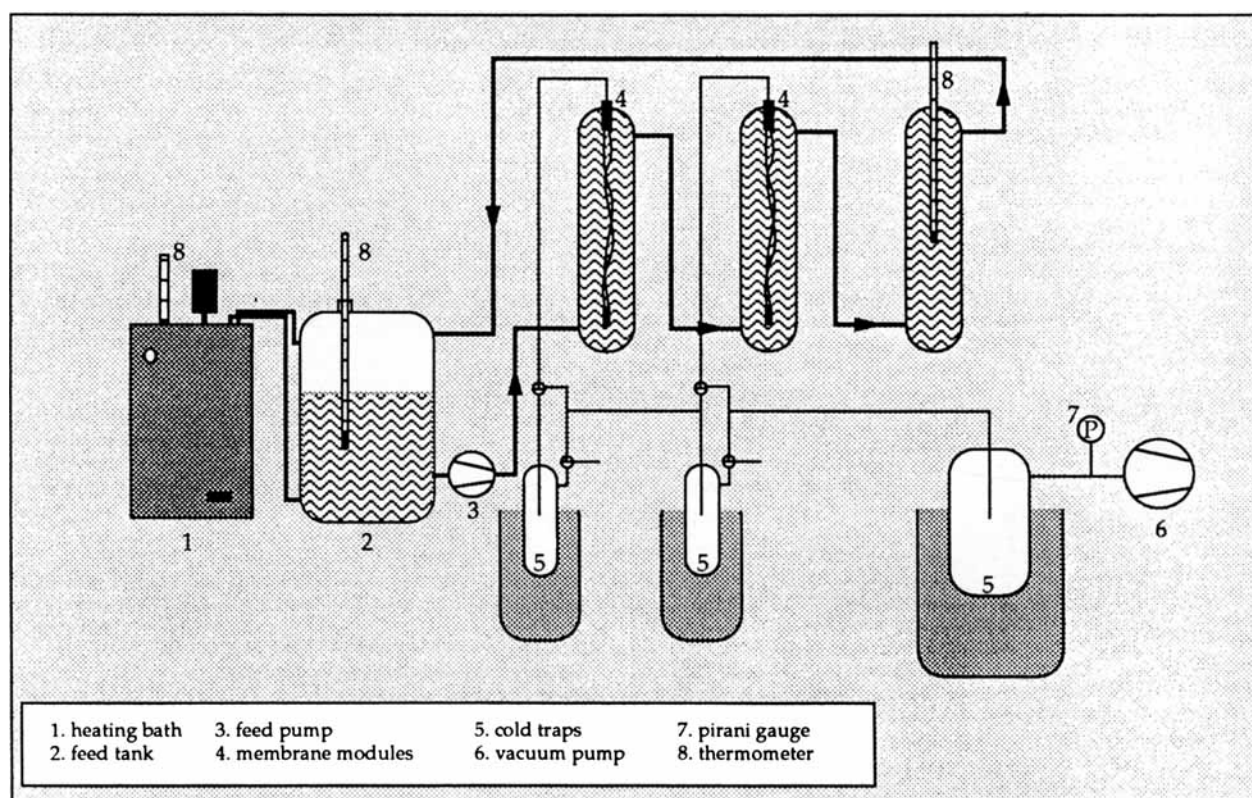


Figure 3 Schematic representation of the pervaporation setup.

**Table I Delay Times of Demixing for a Solution of 35 wt % PSF, 3 wt % Glycerol, and 62 wt % NMP Immersed in Various Nonsolvents, Together with the Viscosity Data of the Nonsolvents Tested**

Nonsolvent	Viscosity (cP)	Delay Time (s)
Glycerol	945	7620
80% Glycerol/20% I-PrOH*	281.4	3900
50% Glycerol/50% I-PrOH	44.7	2303
20% Glycerol/80% I-PrOH	7.8	1491
1-Pentanol	3.31	1545
I-PrOH	2.40	965
Water	1.00	0
Methanol	0.60	0
Ethanol	1.22	0

\* I-PrOH = iso-propanol.  
% = vol %.

A defect-free layer is required to obtain the intrinsic selectivity of the polymer material.

Table I represents the delay times of demixing of several nonsolvents using a polymer solution consisting of 35 wt % PSF, 3 wt % glycerol, and 62 wt % NMP. The viscosities of the nonsolvents are also presented. The viscosity of the iso-propanol/glycerol mixtures is calculated according to the method proposed by Grunberg and Nissan.<sup>24</sup>

Water, methanol, and ethanol as a nonsolvent show instantaneous demixing, while all the other nonsolvents such as pentanol, glycerol, iso-propanol, and mixtures of the latter two show delayed demixing. From the delay times presented in Table I it can be concluded that the largest ratio for solvent outflow/nonsolvent inflow can be achieved in case

a solution of 35 wt % PSF and 3 wt % glycerol in NMP is coagulated in pure glycerol.

In Table II, some pervaporation data are represented for PSF hollow fiber membranes spun with different nonsolvents as the first coagulant and water as the second coagulant. The temperature of the spinning dope was maintained at a temperature of 67°C.

From Table II it can be concluded that going from glycerol to a mixture of 20 vol % glycerol and 80 vol % iso-propanol the selectivity drops using nonsolvents showing shorter delay times (see Table I). The lower selectivities are accompanied by higher fluxes, which is a normal behavior.

The fibers spun with pure glycerol as a first coagulant show the same selectivities and fluxes as when a mixture of 80 vol % glycerol and 20 vol % iso-propanol is used. The highest selectivity is obtained when pentanol is used as a first nonsolvent, but relatively long contact times are necessary to obtain a dense top layer. The lower flux for the pentanol case can be explained by the longer contact time with the first coagulant, which results in a relatively thick top layer.

Considering the ease of spinning, a nonsolvent with a lower viscosity as a first coagulant shows a more continuous and better controllable flow. Because the mixture 80/20 wt % glycerol/iso-propanol results in higher selectivities compared to mixtures that contain higher amounts of iso-propanol and because it is not as dangerous for one's health as pentanol, all the other fibers that are presented in this article have been spun using this mixture as a first coagulant.

SEM pictures (see Fig. 4) of the hollow fiber membranes spun from a solution containing 35 wt

**Table II Selectivity and Flux of PSF Hollow Fiber Membranes for the Dehydration of 80 wt % Acetic Acid in Water at 70°C**

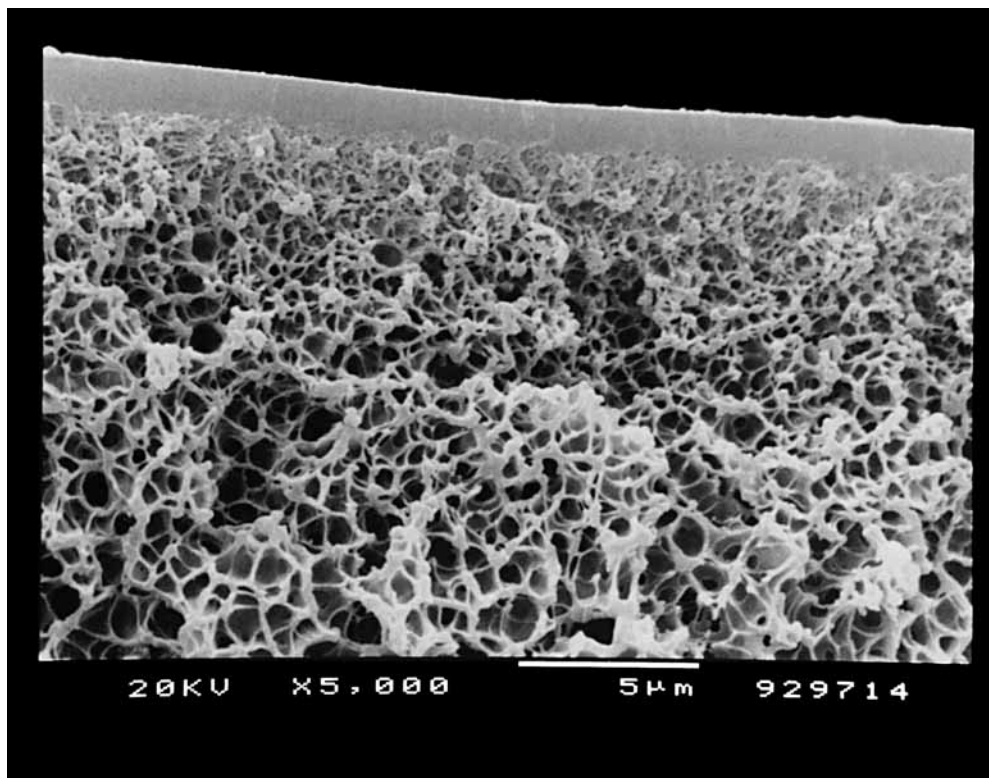
First Nonsolvent Bath	Contact Time 1 <sup>st</sup> Bath(s)	Selectivity	Flux (kg/m <sup>2</sup> h)
Pentanol	5.7	53	0.084
Glycerol	0.82	42	0.130
80% Glycerol/20% I-PrOH <sup>†</sup>	1.12	44.1	0.132
50% Glycerol/50% I-PrOH	1.08	39.6	0.135
20% Glycerol/80% I-PrOH	1.08	32.6	0.170

Fibers are spun using 35 wt % PSF, 3 wt % glycerol, and 62 wt % NMP as a spinning dope and variable first nonsolvents as a first coagulation bath; second coagulation bath: water; bore liquid: water.

\* Intrinsic selectivity of PSF is  $\alpha = 620$ .

<sup>†</sup> I-PrOH = iso-propanol.

% = vol %.



**Figure 4** Cross-section of a PSF hollow fiber membrane; spinning dope: 35 wt % PSF; 62 wt % NMP; 3 wt % glycerol.

% PSF, 3 wt % glycerol, and 62 wt % NMP showed a rather closed cell structure and a relatively dense layer at the bore side [Fig. 9(a)]. These closed cells and dense layer contribute, to a large extent, to the transport resistance, as can be deduced from the relatively low fluxes presented in Table II. According to the SEM picture, the top layer is about  $1.4 \mu\text{m}$  thick, which means that if the substructure had no transport resistance at all the flux should be about  $0.46 \text{ kg/m}^2\text{h}$  instead of  $0.13 \text{ kg/m}^2\text{h}$ , as found experimentally. This can be concluded from permeability data obtained from pervaporation experiments using homogeneous flat sheet PSF membranes and a feed of 80/20 wt % acetic acid/water at  $70^\circ\text{C}$ ; an intrinsic selectivity of  $\alpha = 620$  and an intrinsic permeability of  $p = 0.65 \times 10^{-6} \text{ kg/mh}$  were measured.

#### Effect of Solvent Type

The position of the binodal in a ternary phase diagram for a system polymer/solvent/nonsolvent is dependent on the interactions of solvent and polymer ( $\chi_{23}$ ), nonsolvent and polymer ( $\chi_{13}$ ), and nonsolvent and solvent ( $\chi_{12}$ ). Therefore, the choice of

the solvent and nonsolvent used in the spinning process might be important with respect to membrane formation.

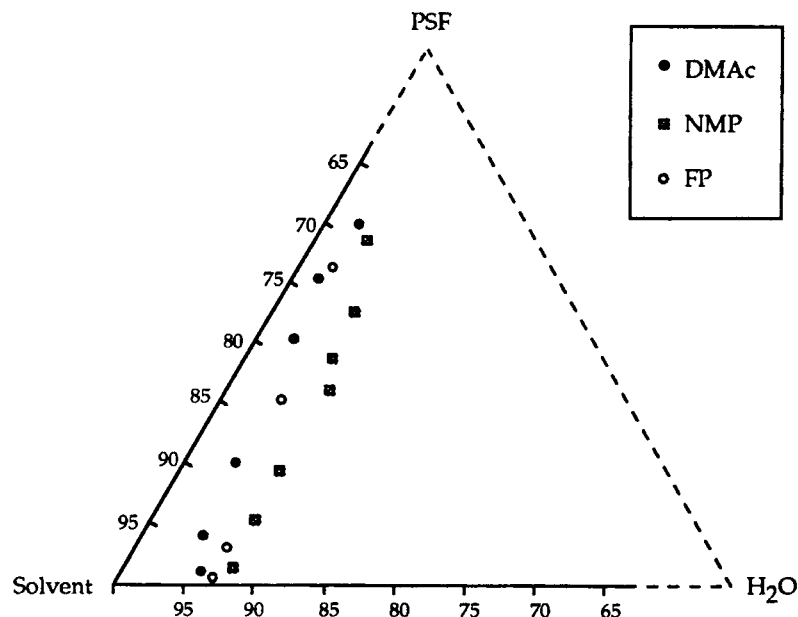
For PSF, various solvents are known. Three different solvents (DMAc, NMP, and FP), all well miscible with water, were used to study the influence of the solvent on the ultimate separation properties of the fibers.

Binodal compositions for the system PSF/solvent/water are represented in Figure 5.

The data for DMAc and NMP are obtained from literature,<sup>25</sup> and the data for FP are determined by cloud point measurements using a simple titration technique as used by others.<sup>26-28</sup>

When the interaction between solvent and nonsolvent decreases ( $\text{DMAc} > \text{FP} > \text{NMP}$ ), the binodals are shifted from the PSF/solvent axis. Figure 5 shows that the binodal composition curves are lying very close together. The interaction parameter,  $\chi_{12}$  for NMP is the highest, and for DMAc, the lowest (a higher interaction parameter means a lower interaction).

The viscosity of solutions of 32% PSF and the molar volumes of the three solvents studied are represented in Table III.



**Figure 5** Ternary phase diagram for the systems: PSF/NMP/H<sub>2</sub>O,<sup>24</sup> PSF/DMAc/H<sub>2</sub>O,<sup>24</sup> and PSF/FP/H<sub>2</sub>O.

Fibers have been spun using a solution of 30 wt % PSF in the three solvents given in Table III. The spinning temperature was 48°C, as first nonsolvent a mixture of 80 vol % glycerol and 20 vol % isopropanol was used, whereas water was used as second nonsolvent and as bore liquid.

The pervaporation results represented in Table IV show similar separation properties for hollow fiber membranes spun from polymer solutions with NMP or DMAc as solvent. Scanning electron microscope pictures of the different fibers show the same membrane structure for NMP (see Fig. 6) and DMAc (see Fig. 7), which might explain their similar separation behavior.

The structures shown in Figures 6 and 7 are typical structures obtained in a dual bath spinning pro-

cess:<sup>18,19</sup> macrovoids are formed from the inside while they are absent from the outside.

From the bore side of the nascent fiber instantaneous liquid-liquid demixing occurs. Obviously, conditions here are favorable for macrovoid formation, following the pattern as explained earlier (theoretical section).<sup>22,23</sup> The macrovoids do not extend over the complete thickness of the fiber wall. Approaching the outside surface, polymer concentrations are increasing (due to loss of solvent to both interfacial regions), and diffusive flow of nonsolvent induces new nuclei to be formed; this stops further growth of macrovoids.

At the outside top layer delayed demixing takes place. Because there is a relatively large outflow of solvent compared to the inflow of nonsolvent, the polymer concentration at the interphase increases and a dense top layer results.

A completely different structure can be observed when FP is used as a solvent (see Fig. 8). This structure shows a few macrovoids formed from the inside, but definitely now macrovoids have formed from the outside. This cannot be explained by a different solvent/water interaction (i.e., by a difference in thermodynamics), because the binodal with FP as solvent lies in between the binodals when NMP or DMAc are used (see Fig. 5). The only difference between DMAc, NMP, and FP is the larger molar volume of the solvent and the high viscosity of the

**Table III** Viscosity Data for Solutions of 32% PSF in Various Solvents and Solvent Molar Volumes

Solvent	Polymer Dope Viscosity (Cps at 30°C)*	Molar Volume (cm <sup>3</sup> /mol)
Formylpiperidine	201,750	111.05
<i>N</i> -methylpyrrolidone	44,000	95.96
Dimethylacetamide	17,300	92.98

\* Data from Kesting et al.<sup>11</sup>



**Table IV Selectivity and Flux of PSF Hollow Fiber Membranes for the Dehydration of 80 wt % Acetic Acid in Water at 70°C**

PSF (wt %)	Solvent	Spinning Temp. (°C)	Contact Time 1° Bath(s)	Selectivity	Flux (kg/m <sup>2</sup> h)
30	NMP	48	0.80	54.1	0.222
30	DMAc	48	0.68	59.8	0.193
30	FP	48	1.28	5.2	0.326

Fibers are spun using various solvents in the spinning dope and no additive.

First nonsolvent: 80/20 vol % glycerol/i-propanol; second nonsolvent: water; bore liquid: water.

polymer solution when FP is the solvent, pointing to possible kinetic effects. At the bore side of the fiber, this might result in an increased ratio of inflow of water compared to solvent outflow by diffusion, so that conditions for the formation of new nuclei will be favored so much that macrovoids are prevented to grow. Also, the phenomena at the outside fiber surface are different when FP is used as the solvent. Because of kinetic reasons (high viscosity of the polymer solution, higher frictional forces for the solvent because of a larger molar volume), the solvent outflow into the first nonsolvent bath is mitigated so much that in the second nonsolvent bath macrovoid formation will get a chance. Because the polymer solution has not increased much in concentration, conditions are quite favorable for macrovoid formation once water has come in to form the first nuclei. The very low selectivity for hollow fibers spun with FP as the solvent might be due to fine pores in the ultrathin top layer as is usually encountered for structures with macrovoids.

When NMP or DMAc are used as solvent, similar high selectivities and reasonable flux values are obtained. Despite the somewhat longer contact time with the first nonsolvent bath in the case of NMP, a higher flux is obtained for the NMP fibers. For all further experiments, NMP is used as solvent.

### Effect of Additive Concentration

To investigate the influence of a nonsolvent-type additive to the polymer solution on the resistance of the sublayer, its effect on the demixing process of the polymer solution and water can be considered. As soon as the bore liquid (water) contacts the polymer solution, the diffusion processes of solvent (NMP) out and nonsolvent (water) into the polymer layer starts. By adding a hydrophilic nonsolvent, like glycerol, to the polymer solution, the inflow of water into the polymer solution will be enhanced.

In addition, the polymer/solvent/additive system lies closer to the binodal, which also favors a more open structure of the sublayer.

Addition of a nonsolvent to the spinning dope can also suppress the formation of macrovoids.<sup>18,23</sup> One should consider, though, that macrovoids as such are not disadvantageous in pervaporation membranes as long as the wall of the voids are open and the fiber has enough mechanical strength.

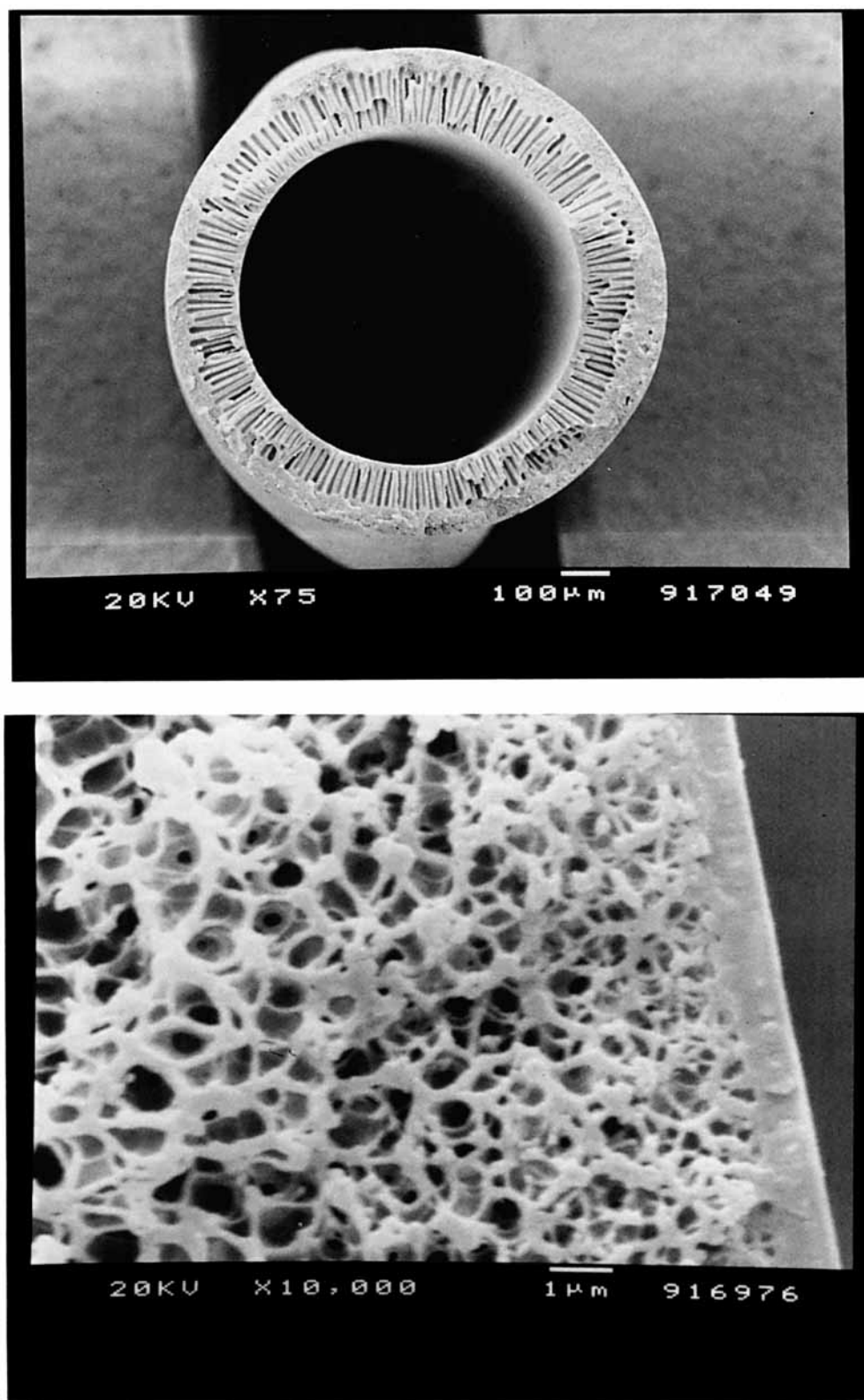
In Table V, pervaporation properties are represented as a function of the amount of glycerol added to the polymer spinning dope. A nice increase in flux can be observed by the addition of glycerol; obviously, a more open substructure is obtained. Furthermore, the results show that the addition of 10 wt % of glycerol is too much; the system polymer/solvent/additive then lies too close to the binodal composition in the ternary phase diagram. Diffusion of a very small amount of solvent into the coagulation bath and/or diffusion of a very small amount of nonsolvent into the outside of the fiber is enough to cross the binodal and result in liquid-liquid demixing, so that a defect-free top layer could not be formed.

### Effect of Polymer Concentration

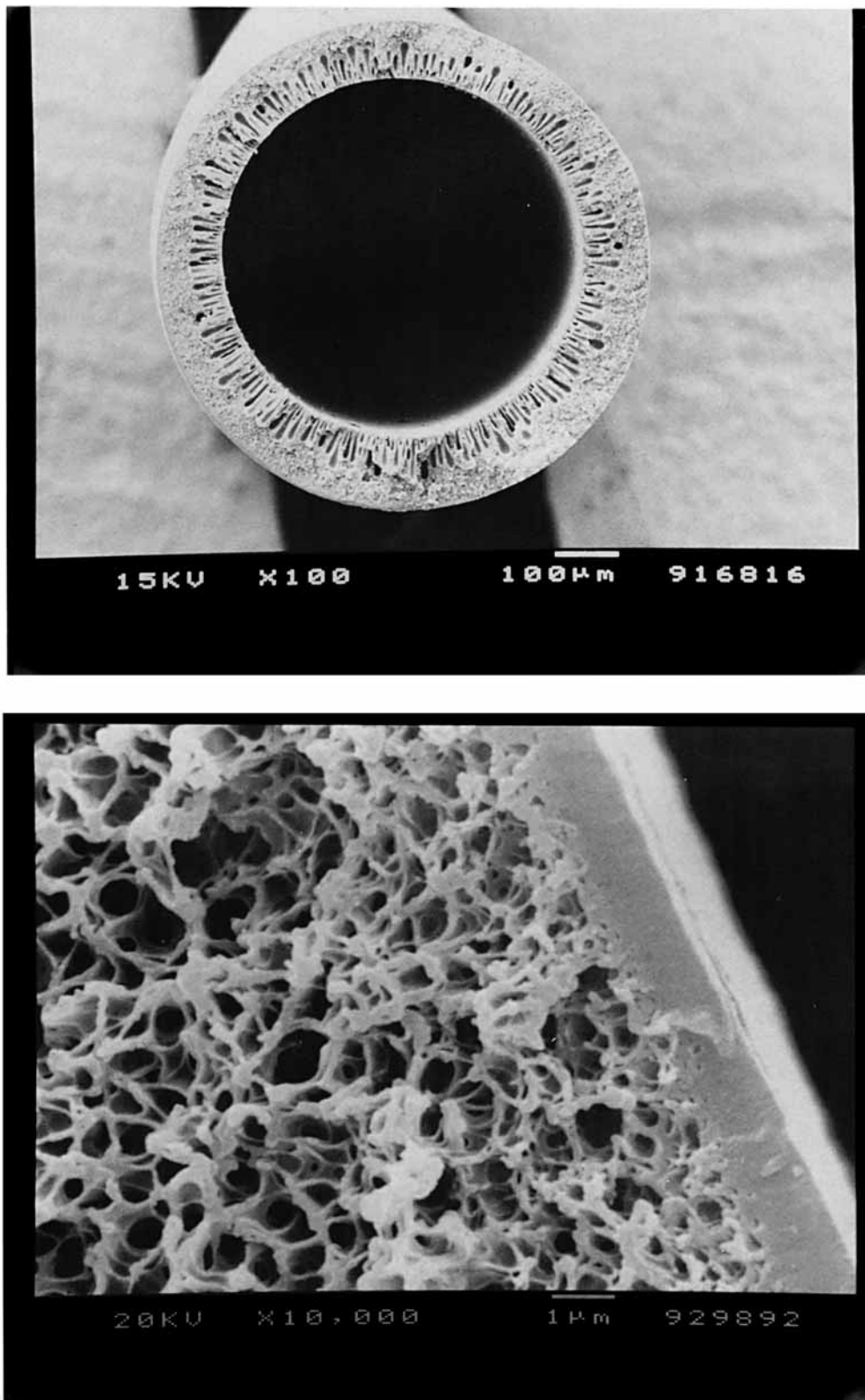
To decrease the resistance of the substructure, the polymer concentration of the spinning dope has been varied. By decreasing the polymer concentration a better interconnectivity of the pores in the substructure is expected. Besides, an increase in number and/or size of macrovoids is expected as well.<sup>23,29</sup> A lower polymer concentration will also influence the density and thickness of the toplayer.

Pervaporation properties of hollow fiber membranes as a function of the polymer concentration are represented in Table VI.

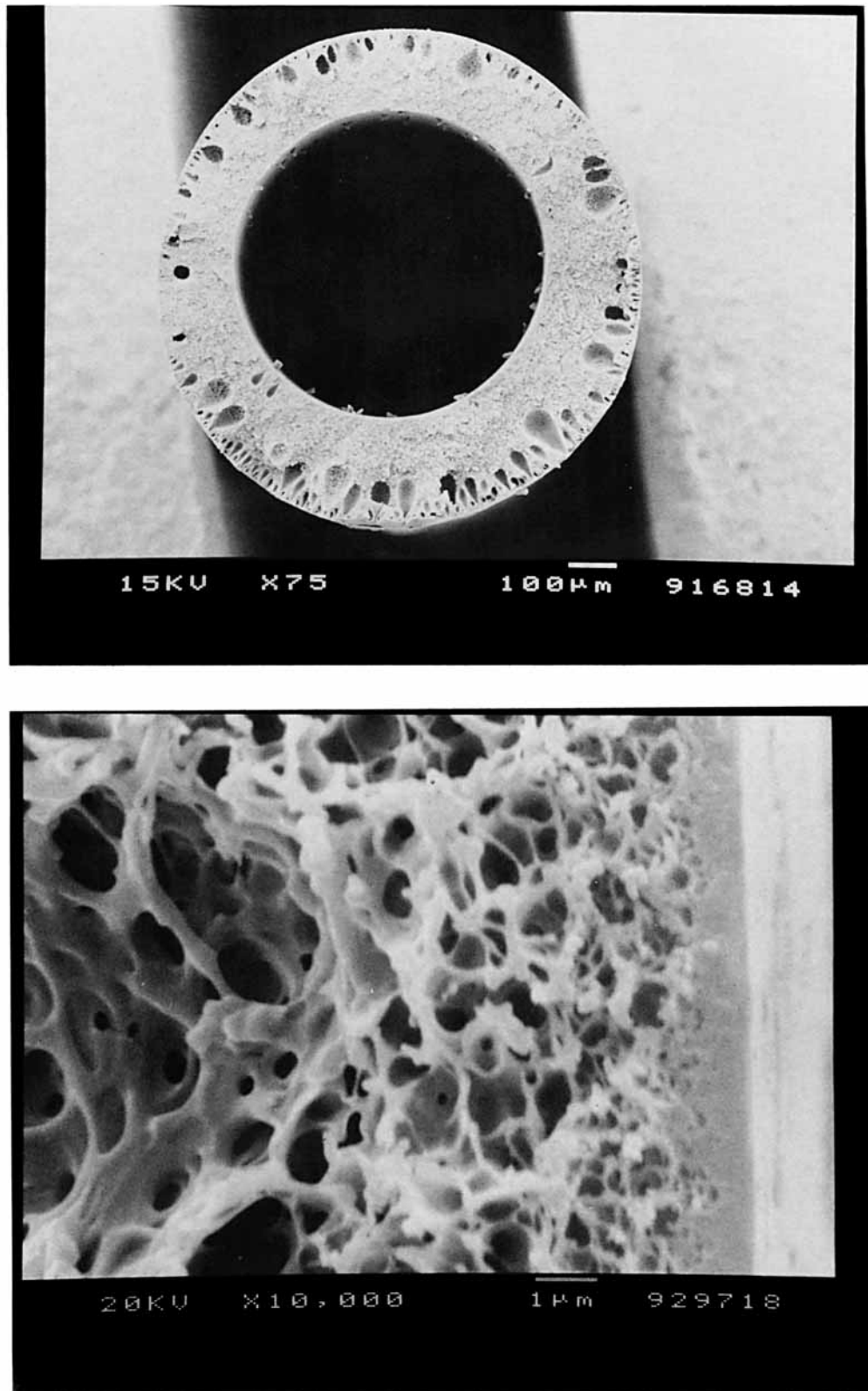
The temperature of the spinning dope during the spinning process was varied with the initial polymer



**Figure 6** Cross-section and top layer of a PSF hollow fiber membrane; spinning dope: 30 wt % PSF; 70 wt % NMP, bore liquid: water first nonsolvent: 80/20 vol % glycerol/i-propanol; second nonsolvent: water.



**Figure 7** Cross-section and top layer of a PSF hollow fiber membrane; spinning dope: 30 wt % PSF; 70 wt % DMAc; bore liquid: water first nonsolvent: 80/20 vol % glycerol/i-propanol; second nonsolvent: water.



**Figure 8** Cross-section and top layer of a PSF hollow fiber membrane; spinning dope: 30 wt % PSF; 70 wt % FP; bore liquid: water first nonsolvent: 80/20 vol % glycerol/i-propanol; second nonsolvent: water.

**Table V Selectivity and Flux of PSF Hollow Fiber Membranes for the Dehydration of 80 wt % Acetic Acid in Water at 70°C as a Function of the Glycerol Concentration in the Spinning Dope**

PSF (wt %)	Glycerol (wt %)	NMP (wt %)	Spinning Temp. (°C)	Contact Time 1° Bath(s)	Selectivity	Flux (kg/m <sup>2</sup> h)
30	0	70	48	0.80	54.1	0.222
30	5	65	48	0.80	65.0	0.285
30	7	63	49	0.82	63.4	0.334
30	10	60	47	0.97	2.5	1.05

First nonsolvent: 80/20 vol % glycerol/i-propanol; second nonsolvent: water; bore liquid: water.

**Table VI Selectivity and Flux of PSF Hollow Fiber Membranes for the Dehydration of 80 wt % Acetic Acid in Water at 70°C as a Function of the Polymer Concentration in the Spinning Dope, with and without Glycerol as Additive**

PSF (wt %)	Glycerol (wt %)	NMP (wt %)	Spinning Temp. (°C)	Contact Time 1° Bath(s)	Selectivity	Flux (kg/m <sup>2</sup> h)
35	0	65	48	0.73	47.1	0.171
30	0	70	48	0.80	54.1	0.222
25	0	75	27	0.70	52.6	0.341
30	7	63	49	0.79	63.4	0.334
27.5	7	65.5	25	0.73	71.6	0.464
25	7	68	25	0.91	63.5	0.511

First nonsolvent: 80/20 vol % glycerol/i-propanol; second nonsolvent: water; bore liquid: water.

**Table VII Selectivity and Flux of PSF Hollow Fiber Membranes for the Dehydration of 80 wt. % Acetic Acid in Water at 70°C as a Function of the Solvent (NMP) Concentration in the Bore Liquid (H<sub>2</sub>O)**

Spinning Dope			Bore Liquid		Contact Time 1° Bath(s)	Selectivity	Flux (kg/m <sup>2</sup> h)
PSF (wt %)	Glycerol (wt %)	NMP (wt %)	H <sub>2</sub> O (wt %)	NMP (wt %)			
35	3	62	100	0	1.12	44.1	0.132
35	3	62	40	60	1.08	45.9	0.141
35	3	62	35	65	1.03	44.0	0.240
35	3	62	30	70	1.18	54.0	0.374

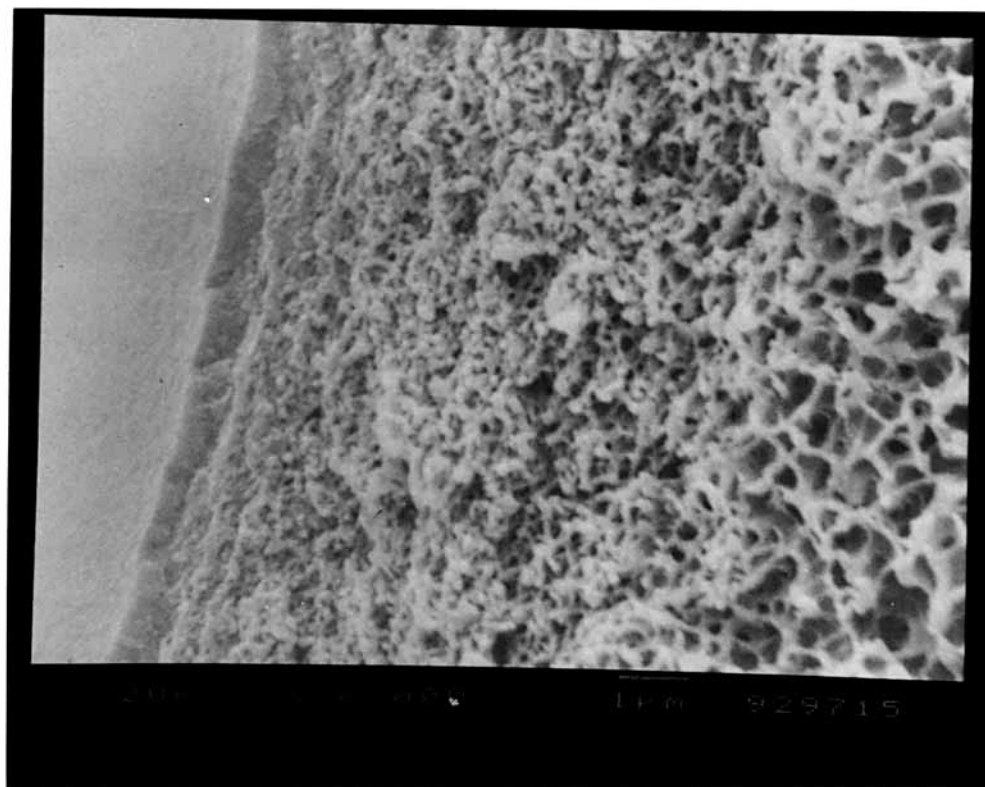
First nonsolvent: 80/20 vol % glycerol/i-propanol; second nonsolvent: water.

concentration because a certain minimum viscosity is necessary for a constant extrusion rate of the spinning dope.

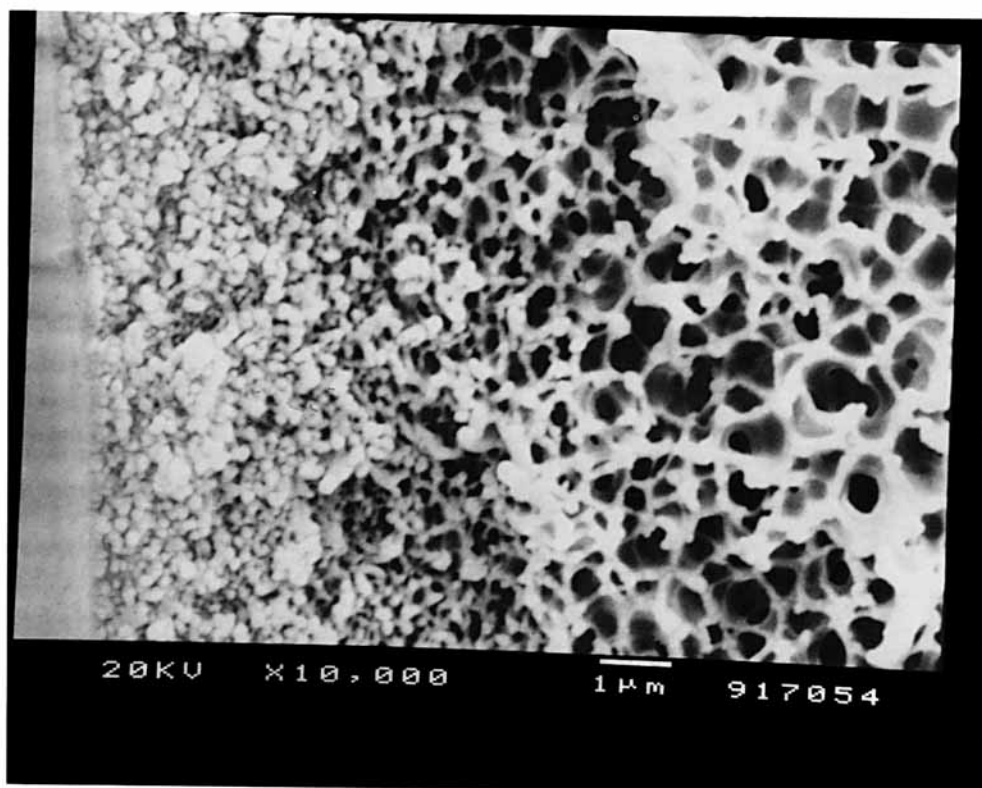
Table VI shows a clear increase in flux using lower polymer concentrations in the spinning dope. Addition of glycerol as additive gives an extra increase

in flux compared to the dopes where no glycerol was used. The lower polymer concentration results in a more open, porous substructure.

Besides giving a higher flux, the selectivity of the fibers spun with glycerol in the spinning dope is increased as well.

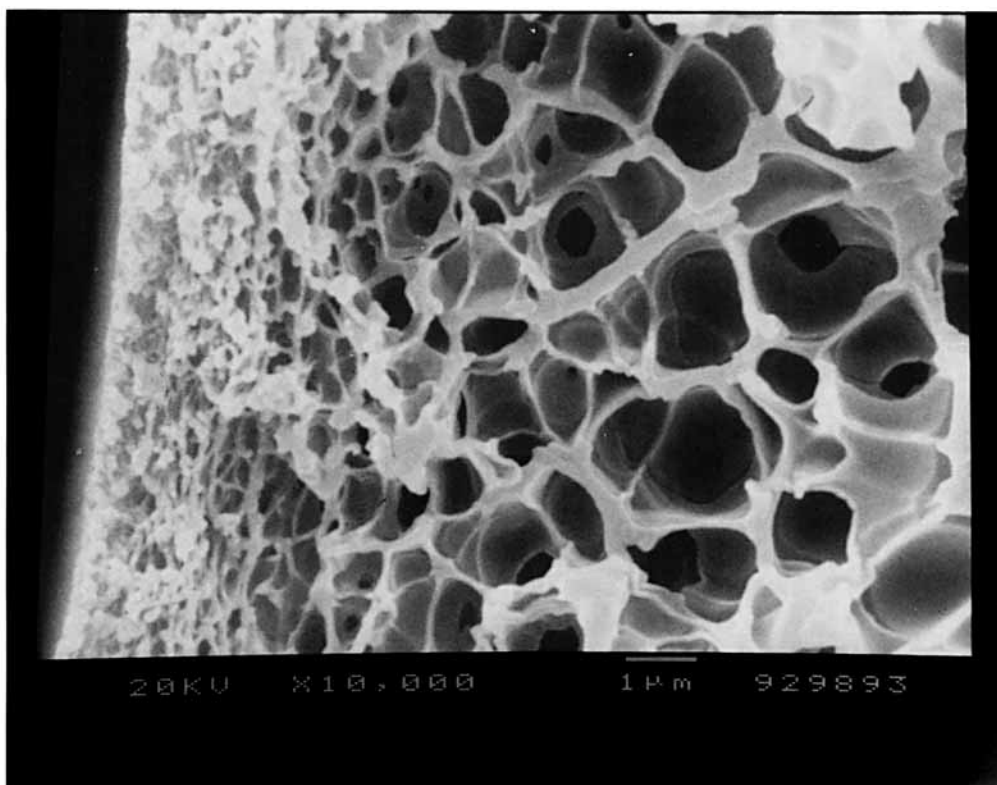


(a)

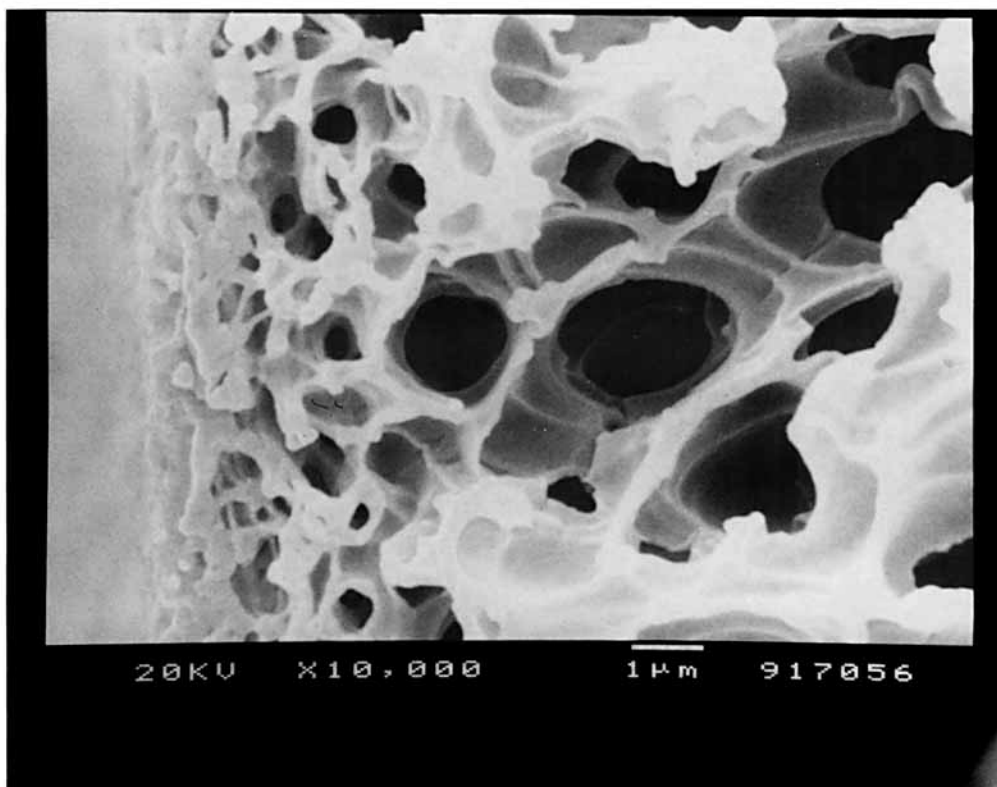


(b)

**Figure 9** Top layer structure at the bore side of the PSF hollow fiber membrane as a function of the ratio NMP/H<sub>2</sub>O in the bore liquid; spinning dope: 35 wt % PSF; 62 wt % NMP; 3 wt % glycerol; first nonsolvent: 80/20 vol % glycerol/i-propanol; second nonsolvent: water. (a). Bore liquid: 100% H<sub>2</sub>O; (b) bore liquid: 30% H<sub>2</sub>O/70% NMP; (c) bore liquid: 25% H<sub>2</sub>O/75% NMP; (d) bore liquid: 20% H<sub>2</sub>O/80% NMP.

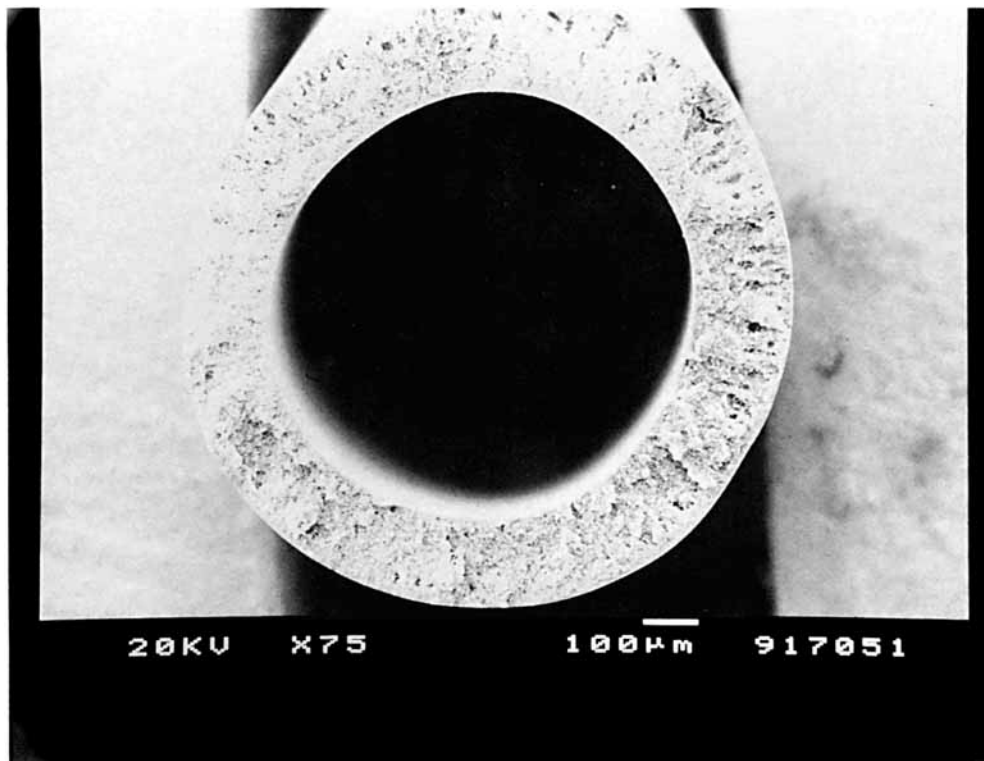


(c)

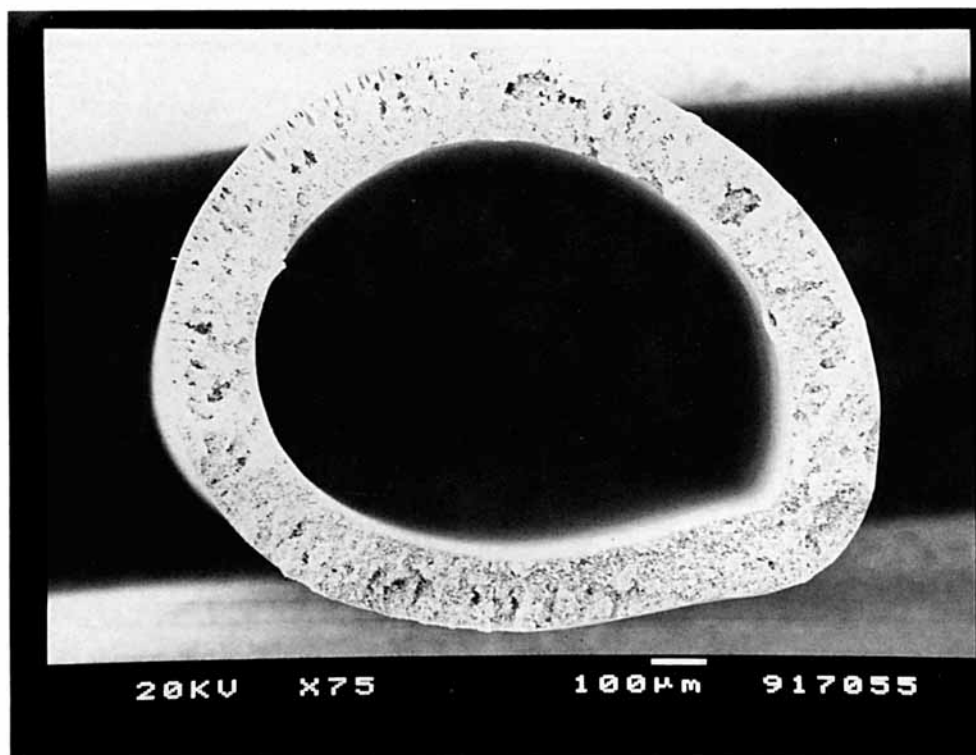


(d)

**Figure 9** (Continued from the previous page)



(a)



(b)

**Figure 10** Cross-section of a PSF hollow fiber membrane spun with 75 wt % NMP (left) and 80 wt % NMP (right) in water as bore liquid; first nonsolvent: 80/20 vol % glycerol/i-propanol; second nonsolvent: water. (a) 25 wt % water/75 wt % NMP; (b) 20 wt % water/80 wt % NMP.



### Effect of Bore Liquid Composition

From SEM pictures it can be clearly seen that the layer formed at the inside of the hollow fiber is quite dense compared to the rest of the structure [see Fig. 9(a)]. The higher the polymer concentration in the spinning dope the denser this layer and, consequently, the higher the resistance will be. In order to reduce this resistance, different ratios of NMP/water were used as the bore liquid. The results of these experiments are represented in Table VII.

Table VII shows a significant increase in flux when increasing the amount of NMP in the bore liquid while the selectivity remains almost constant. Scanning electron microscope pictures are represented in Figure 9.

From Figure 9 it can be concluded that the rather dense layer at the bore side, obtained when pure water is used as bore liquid, is getting more open when the solvent concentration in the bore liquid is increased.

Figure 10 shows that it is not possible to increase the NMP concentration in the bore liquid up to 80 wt % because the spinning process cannot be controlled anymore and the fibers lose their shape. In the first part of the spinning process the nascent fiber is in contact with the first nonsolvent where no coagulation takes place. At the same time, due to the high concentration of NMP in the bore liquid, delayed demixing at the hollow fiber bore will occur as well.

During a short period of time the nascent fiber has no mechanical strength at all and will elongate due to gravitation and other forces (e.g., difference in spinning rate over winding rate). Consequently, by the time the nascent fiber reaches the first guiding wheel in the second coagulation bath of the spinning setup the solidification is not completed, resulting in fibers without a perfect round shape (Fig. 10).

Although the selectivities of the PSF hollow fiber membranes are acceptable ( $\alpha = 65\text{--}80$ ) they never reached the intrinsic value of  $\alpha = 620$ , measured for homogeneous flat membranes of a thickness of 20  $\mu\text{m}$ . The reason for this phenomenon will be discussed elsewhere.<sup>30</sup> In the appendix, it will be shown that the loss in selectivity cannot be attributed to a reduction in driving force due to resistances in the sublayer and the bore of the fiber.

### CONCLUSIONS

From the results presented it can be concluded that PSF hollow fiber membranes with relatively high

fluxes and acceptable selectivity can be produced in one step by the dual bath spinning process. The modification of the spinneret makes this process very easy to control and, therefore, excellently applicable for large scale production.

Furthermore, it can be concluded that the flux of the PSF hollow fiber membranes could be increased by lowering the polymer concentration in the spinning dope to a certain extent, increasing the concentration of glycerol in the spinning dope (again to a certain extent), and increasing the concentration of NMP in the bore liquid (also to a certain extent).

A mixture of 80 vol % glycerol and 20 vol % isopropanol appeared to be a suitable first nonsolvent to densify the outer layer of the fibers. Highly selective membranes could be obtained and the viscosity of the mixture was low enough to give a constant flow profile of the nonsolvent around the nascent fiber.

The best results obtained for the dehydration of 80 wt % acetic acid at 70°C are fibers with a flux of 0.511 kg/m<sup>2</sup>h and a selectivity of  $\alpha = 63.5$  and fibers with a flux of 0.464 kg/m<sup>2</sup>h and a selectivity of  $\alpha = 71.6$  using a spinning dope of 25 wt % PSF, 7 wt % glycerol, and 68 wt % NMP, or 27.5 wt % PSF, 7 wt % glycerol, and 65.5 wt % NMP, respectively.

### APPENDIX

#### App. I: Pressure Loss in the Bore of a Hollow Fiber

Consider a hollow fiber pervaporation module in which the feed is introduced at the outside of the fibers and the permeate is collected by applying a vacuum at the bore side of the fibers. A reduction of flux can take place due to pressure loss inside the bore along the fiber. Whether pressure loss occurs depends on the membrane flux, the length of the hollow fiber, and the bore diameter.

Gooding et al.<sup>A.1</sup> developed a model to calculate the pressure at the dead end (when fibers are sealed at one end) of a hollow fiber membrane having a certain flux as a function of the fiber length and the bore diameter.

The model assumes an ideal gas behavior of the permeate and is based on the steady-state mechanical energy balance (Bernoulli)

$$2v \frac{dv}{dz} + \frac{1}{\rho} \frac{dp}{dz} + \frac{2fv^2}{d} = 0 \quad (\text{A1})$$

**Table A.1 Dead End Pressure and Flux at Dead End Pressure as a Function of the Total Flux**

$K$ (flux at $p_L$ ) (kg/m <sup>2</sup> h)	$A$	$B$	$p_L$ (mmHg)	$p_0$ (mmHg)	Flux at $p_0$ (kg/m <sup>2</sup> h)
0.2	$1.488 \times 10^{-2}$	$9.842 \times 10^{-6}$	0.5	14.1	0.195
0.5	$1.488 \times 10^{-2}$	$2.460 \times 10^{-5}$	0.5	22.3	0.471
0.7	$1.488 \times 10^{-2}$	$3.445 \times 10^{-5}$	0.5	26.4	0.643
1.0	$1.488 \times 10^{-2}$	$4.921 \times 10^{-5}$	0.5	31.7	0.883

$\mu_{H_2O} = 1.05 \times 10^{-3} \text{ kg}^2/\text{ms}$        $R = 8.314 \text{ J/mol} \cdot \text{K}$   
 $M_{H_2O} = 18 \times 10^{-3} \text{ kg/mol}$        $T = 323 \text{ K}$   
 $p_{sH_2O} = 1.2334 \times 10^4 \text{ N/m}^2 (50^\circ\text{C})$        $L = 0.2 \text{ m}$   
 $d = 5 \times 10^{-4} \text{ m}$

and a steady-state differential mass balance on a single fiber

$$j\pi d = \frac{dm}{dz} \quad (\text{A2})$$

By substituting  $m$  in terms of the radially average velocity  $v$  and the mass density  $r$  of the permeate, relation (A2) can be expressed by

$$p \frac{dv}{dz} + v \frac{dp}{dz} = \frac{4RTj}{Md} \quad (\text{A3})$$

Cross-substitution of the pressure and velocity derivatives and the introduction of dimensionless variables results in the relation for the dead end pressure,  $P_0$ :

$$P_0 = \left[ P_L^2 + A \cdot B \cdot \left( \frac{L}{d} \right)^2 \cdot (1 - P_L^2) \right]^{0.5} \quad (\text{A4})$$

with

$$A = \frac{16\mu}{dp_s} \sqrt{\frac{2RT}{M}} \text{ dimensionless friction parameter}$$

$$B = \frac{4K}{p_s} \sqrt{\frac{2RT}{M}} \text{ dimensionless flux parameter}$$

$$P = \frac{p_L}{p_s}$$

$$P_0 = \frac{p_0}{p_s}$$

For the fibers studied here, the pressure at the dead end of the hollow fiber can be calculated as a function of the permeate flux. The bore diameter of the fibers is about 0.5 mm and the length of the fibers in the modules was about 20 cm. The permeate was considered as pure water. In Table A.1, the dead end pressure  $p_0$  and the flux reduction at  $p_0$  are represented as a function of the permeate flux at a temperature of 50°C. Using relation (A5) the flux at pressure  $p$  can be calculated.

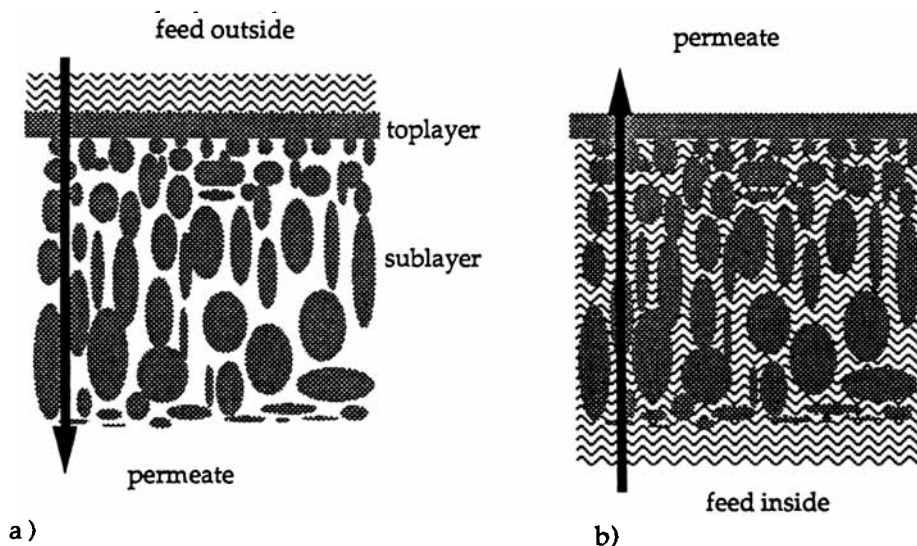
$$J(p) = K \left( 1 - \left( \frac{p}{p_s} \right)^2 \right), \quad (\text{A5})$$

From Table A.1 it can be concluded that when a flux of 0.5 kg/m<sup>2</sup>h is obtained, the flux at the dead end of the fiber is only 5.8% lower than at the beginning of the fiber. Therefore, a loss of the driving force due to pressure loss inside the bore of the fibers studied can be neglected. However, it is clear that hollow fiber membranes for pervaporation will have optimal dimensions, which means short modules with capillary type of fibers.

#### App. II: The Resistance of the Sublayer

Besides pressure loss in the bore, there can also be a pressure loss in the porous sublayer. Due to the presence of closed cells and/or small pores, the sublayer will have a certain resistance and, therefore, pressure loss in this layer might result in a reduction of the driving force.

To get an impression of this resistance, two permeation experiments have been carried out: one with pure water at the inside of the fiber and one with



**Figure A.1** Schematic representation of a pervaporation experiment with pure water. (a) Feed at the outside; (b) feed at the inside.

pure water at the outside of the fiber. In Figure A.1, a schematic representation of both experiments is represented.

From the pure water flux data the membrane resistance can be calculated using the equation:

$$J_{\text{H}_2\text{O}} = \frac{1}{R_{\text{H}_2\text{O}}} (P_{\text{feed}} - P_{\text{perm}}) \quad (\text{A6})$$

$$\text{where: } P_{\text{feed}} = C_{\text{H}_2\text{O}} \cdot \gamma_{\text{H}_2\text{O}} \cdot P_{s,\text{H}_2\text{O}}$$

$$P_{\text{perm}} = 0 \text{ N/m}^2$$

$$P_{s,\text{H}_2\text{O}} = 2.64 \times 10^3 \text{ N/m}^2$$

$$C_{\text{H}_2\text{O}} = 1$$

$$\gamma_{\text{H}_2\text{O}} = 1$$

It is assumed that the membrane surface area  $A$  at the outside is the same as at the inside. The results

**Table A.2** Pure Water Flux and the Resistance of the Sublayer of Asymmetric PSF Hollow Fiber Membranes at Room Temperature; Duplo Measurements

Feed 100% Water	Feed Outside	Feed Inside
Flux (g/m <sup>2</sup> h)	63	77
	62	78
Membrane resistance (m/s)	$4.19 \times 10^4$	$3.43 \times 10^4$
	$4.26 \times 10^4$	$3.38 \times 10^4$

of the pervaporation experiment as well as of the calculated membrane resistances are represented in Table A.2.

When the feed is at the inside, it is assumed that it will enter the porous layer until it reaches the dense toplayer (see also Fig. A.1). This assumption offers the possibility to calculate the resistance of the toplayer (feed inside). When the feed is at the outside, the calculated resistance consists of the resistance of the toplayer plus the resistance of the sublayer. From the resistance data in Table A.2 it can be calculated that the resistance of the sublayer is  $19\% \pm 1\%$  of the total resistance.

It is unlikely that due to this extra resistance the selectivity decreases from 620 to 60–80.

#### List of Symbols

		dimensions
$A$	dimensionless friction parameter	
$A$	membrane surface area	m <sup>2</sup>
$B$	dimensionless flux parameter	
$C$	concentration in the feed mixture (mol fraction)	
$d$	bore (inside fiber) diameter	m
$j$	mass flux based on the inside surface area	kg/m <sup>2</sup> s
$f$	Fanning friction factor	
$\gamma$	activity coefficient	
$K$	optimum flux at permeate pressure zero	kg/m <sup>2</sup> h
$L$	fiber length	m

$m$	permeate mass flow rate	kg/s
$M$	molecular weight	kg/mol
$p$	pressure	N/m <sup>2</sup>
$p_0$	pressure at the dead end of a hollow fiber	N/m <sup>2</sup>
$p_L$	pressure at the fiber mouth	N/m <sup>2</sup>
$P_s$	saturation pressure	N/m <sup>2</sup>
$\rho$	density	Kg/m <sup>3</sup>
$R$	gas constant	J/mol K
$R_{H_2O}$	water transport resistance	m/s
$T$	temperature	K
$\mu$	viscosity	kg/ms
$v$	velocity	m/s
$z$	distance	m

### indices

feed feed side                      perm. permeate side

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