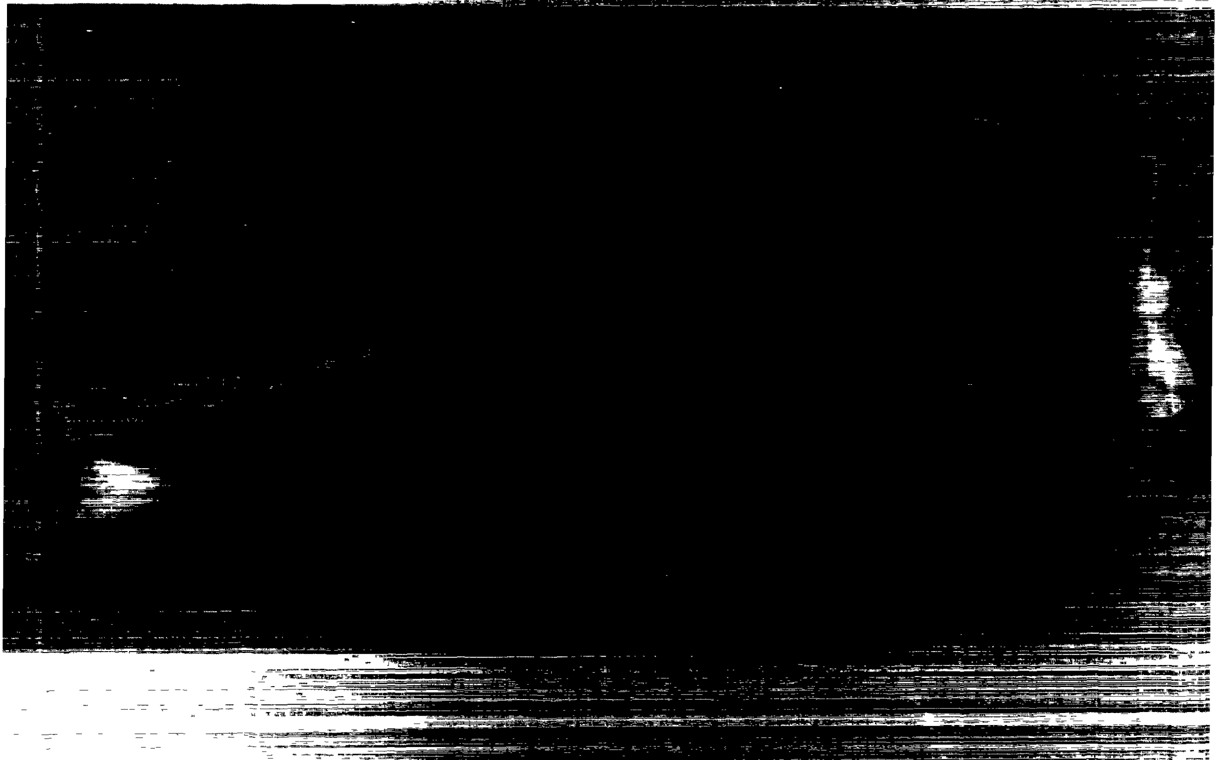
DEHYDRATION OF ACETIC ACID BY PERVAPORATION

Material Science Aspects



Geert-Henk Koops

23

DEHYDRATION OF ACETIC ACID BY PERVAPORATION
Material Science Aspects

PROEFSCHRIFT

ter verkrijging van
de graad van doctor aan de Universiteit Twente,
op gezag van de rector magnificus,
prof. dr. ir. J.H.A. de Smit,
volgens besluit van het College van Dekanen
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door

Geert-Hendrik Koops

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te Ommen

Dit proefschrift is goedgekeurd door de promotor prof. dr. C.A. Smolders en de assistent-promotor dr. ing. M.H.V. Mulder.

VOORWOORD

Het feit dat slechts één naam op de voorkant van dit proefschrift staat vermeld als auteur doet ten onrechte vermoeden dat het hier beschreven werk alléén door die éne persoon tot stand gekomen is. Vele mensen hebben hieraan een bijdrage geleverd, ook mensen die zich dat wellicht niet direct realiseren. Daarom wil ik bij deze graag een ieder hartelijk danken voor zijn of haar bijdrage en in het bijzonder:

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1

ACETIC ACID/WATER SEPARATION BY MEMBRANES

an introduction

ACETIC ACID

Acetic acid has become an important commodity product in the chemical industry with a production capacity of about 4 million tonnes per year worldwide. A survey of the acetic acid market sectors is presented in figure 1. [1,2].

Most of the acetic acid produced is used for the production of vinyl acetate, a basic product for vinyl plastics (like polyvinylacetate, polyvinylalcohol, and polyvinylbutyral), hot-melt adhesives, textile finishes and latex paints. A rapid growth of the vinyl acetate market in the sixties and seventies could be observed due to the synthetic fiber demand.

The second large use of acetic acid is for the production of acetic anhydride, which is an intermediate for the production of cellulose acetate (transparent sheets, photo films, lacquers, etc.), pharmaceuticals and plasticizers.

Furthermore, acetic acid is used as a solvent in the liquid phase oxidation of p-xylene to terephthalic acid and for the production of acetate esters (methyl acetate, ethyl acetate, butyl acetate, etc.) which are also widely used as solvents.

Chloroacetic acid is used in the production of carboxymethyl cellulose and in herbicides, and acetate salts like sodium acetate and ammonium acetate are also products of acetic acid.

The chemical processes for the production of these end-products and intermediates are always accompanied by waste- and/or recycle streams containing acetic acid/water mixtures. In addition, the synthesis of acetic acid itself (carbonylation of methanol [2,3]) results in the production of water as a by-product which has to be removed in order to fulfil the standards of glacial acetic acid ($\geq$ 99.5 wt.% acetic acid [2]). Therefore, the separation of acetic acid and water has become an important separation topic in the chemical industry.

All possible acetic acid/water mixture compositions can be obtained as waste- or recycle stream and depending on the composition range of the mixture some separation techniques are more favourable than others. Techniques industrially used nowadays are [1]:

- Fractionation distillation
- Azeotropic distillation
- Liquid-liquid extraction
- Others, like extractive distillation, carbon adsorption, etc.

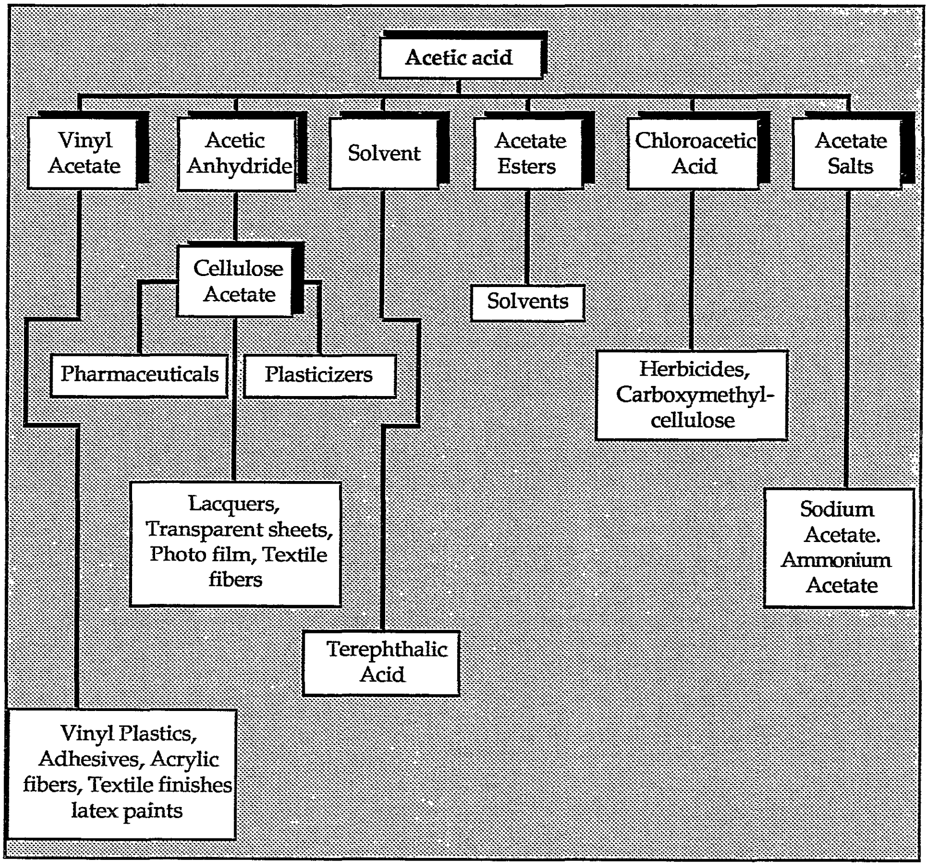


Figure 1 *The acetic acid market sectors*

The straight distillation process consumes much energy. Water (boiling point: 100°C) and acetic acid (boiling point: 117.8°C) do not form an azeotropic mixture, but due to the close boiling points (see the vapour-liquid equilibrium curve, figure 2) a large numbers of trays and a high reflux ratio are necessary to obtain glacial acetic acid.

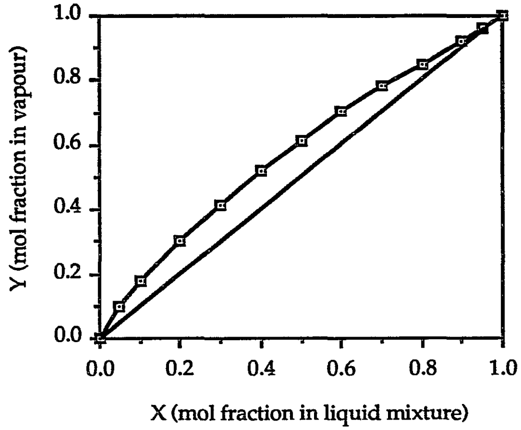


Figure 2 *Vapour-liquid equilibrium, acetic acid/water at 80 °C* (data from [4])

Today, azeotropic distillation is commonly used as an alternative technique for fractionation distillation to remove water from acetic acid in mixtures containing more than 50 wt.% acetic acid. This technique involves the addition of an extra component, a so called entrainer. The entrainer, relatively immiscible with water reduces the effective boiling point of water and carries the water overhead in the distillation column. After condensation of the overhead product the entrainer can be separated from the water due to phase separation and returned to the distillation column.

For mixtures containing 5 to 50 wt.% acetic acid liquid-liquid extraction is normally used, often followed by azeotropic distillation. This process consumes large amounts of energy, especially at low acetic acid concentrations, necessary for the recovery of the extractive solvents by distillation. The same type of solvents are used in liquid-liquid extraction as are used as entrainer in azeotropic distillation, like low molecular weight esters, ethers and ketones.

Other techniques that are not so commonly used for the recovery and concentration of acetic acid/water mixtures are: extractive distillation, carbon adsorption, trioctylphosphine oxide (TOPO) extraction and last but not least membrane separation. A recent study by SRI international [5] even showed that 3.2 trillion KJ/year of energy can be saved for the dehydration of acetic acid when membranes are used in combination with the conventional techniques discussed here.

MEMBRANE SEPARATION

Membranes in General

Considering that the first membrane experiments have already been carried out in the 18th century, using membranes of animal origin, industrial membrane separation is a rather young technology. Only since the last 25 years membrane technology has been strongly developed. In the first place, this growth can be attributed to the development of the asymmetric membrane by Loeb and Sourirajan [6] in the early sixties and secondly to the development and production of new polymers in the last decades.

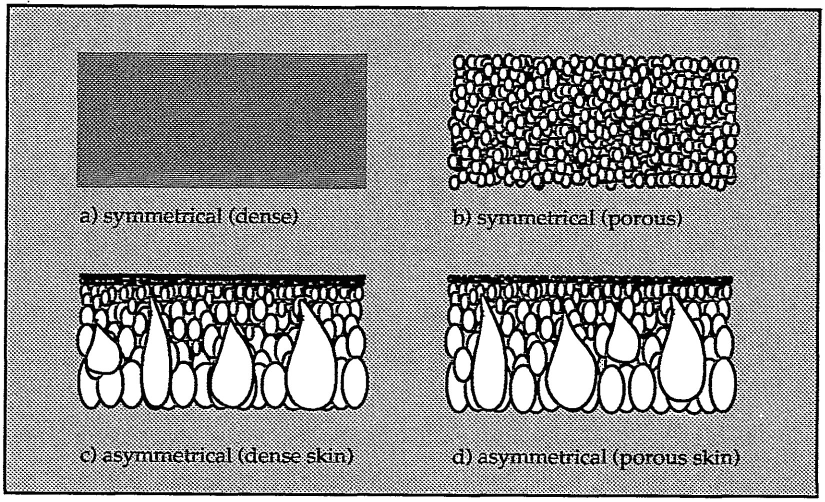


Figure 3 *Membrane structures: a). symmetric, dense; b). symmetric porous; c). asymmetric, dense toplayer; d). asymmetric, dense toplayer*

Asymmetric membranes are advantageous compared to symmetric membranes because the flux determining toplayer is thin, while the sublayer is responsible for the mechanical strength. A schematic representation of symmetric and asymmetric membranes is given in figure 3.

The preparation method of asymmetric membranes offers the possibility of optimizing the membrane separation properties by varying the preparation parameters. Moreover, the introduction into the market of newly developed polymers, like e.g. polyphenyleneoxide (1964), polysulfone (1965), polyether-ether-ketone (1980) and polyetherimide (1982) offers researchers even more possibilities for membrane development.

These developments resulted in the commercialization of membrane modules for microfiltration, ultrafiltration and reverse osmosis (hyperfiltration). These membranes are characterized by the presence of *pores* in the toplayer. The pore size determines the selectivity and a pressure difference across the membrane is responsible for the driving force. The separation mechanism in microfiltration and ultrafiltration is based on a difference in particle size of the components in the feed solution compared to the pore size in the membrane. Typical pore sizes of microfiltration membranes are in the range of 0.1-1 μm (suspensions and microorganisms) and the pores in ultrafiltration membranes are in the range of 0.005-0.1 μm (colloids and macromolecules). In the case of reverse osmosis the pores are so small that the separation is not based on a size exclusion mechanism anymore. These membranes are used to separate particles of the same size, like salt from water in the desalination of seawater or brackish water for the production of drinking water. Nowadays, microfiltration, ultrafiltration and reverse osmosis membrane systems are commercially available in a large variety of membrane materials and suppliers.

Nonporous membranes are developed to accomplish the separation of liquid mixtures (pervaporation), vapour mixtures (vapour permeation) and gas mixtures (gas separation). Here, the separation mechanism is determined by the difference in solubility in and diffusivity through the membrane material. The driving force for separation is a partial pressure difference or chemical potential difference across the membrane. For some applications membrane development has reached the industrial stage, like dehydration of alcohols by pervaporation, hydrogen recovery and nitrogen enrichment of air for cleaning ship holds (no danger of dust explosion due to the absence of oxygen) and for blanketing stored fruit to increase its tenability and quality.

Liquid membranes may be considered as the membranes of the future. These membranes consist of a liquid which is immobilized into the pores of a porous support. A carrier is dissolved in this liquid which facilitates the transport of one of the components from the feed side to the strip side. A major problem with these liquid membranes is their (in)stability in time. The development of these membranes is still in an early stage.

A completely different class of membranes are the ceramic membranes. These membranes are characterized by a very high chemical and thermal resistance and they were developed at the end of the fifties for the enrichment of uranium. Nowadays, ceramic membranes are also developed and applied for industrial microfiltration and ultrafiltration applications. Ceramic membranes are advantageous in cases where the resistance of polymeric membranes is insufficient, e.g. high temperature reactions.

Other membrane processes of interest which have not further been discussed are: dialyses, electrodialyses, nanofiltration, membrane distillation, membrane extraction, and membrane reactors.

Advantages of membrane filtration compared to the more conventional separation techniques like distillation, extraction and carbon adsorption, are among others: a low energy consumption, the separation can be carried out continuously, up-scaling is relatively simple and in principle membrane technology can be used for any kind of separation.

There are certainly disadvantages. The life time of many membranes is still too short, the thermal and chemical resistance of polymeric membranes is often insufficient and especially in microfiltration, ultrafiltration and reverse osmosis membrane applications fouling results in flux decline.

Pervaporation

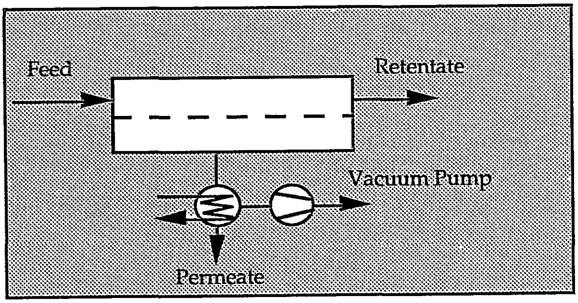
Pervaporation is a membrane separation process where two or more components in the liquid phase are separated by a nonporous membrane. Transport occurs due to a chemical potential gradient across the membrane.

According to the solution-diffusion model separation takes place in three steps:

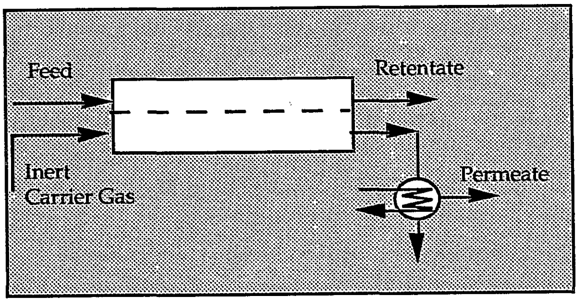
- selective sorption of the components at the feed side
- selective diffusion of the components through the membrane

- desorption of the components at the permeate side

The driving force is a chemical potential gradient across the membrane. This is normally achieved by creating a lower partial pressure at the permeate side compared to the feed side, either by applying a vacuum or by using an inert carrier gas at the permeate side (see figure 4). The permeated product is removed as vapour and must be condensed.



4 a. vacuum



4 b. inert carrier gas

Figure 4 *Pervaporation with a) a vacuum at the permeate side; b) a carrier gas at the permeate side*

Pervaporation is an attractive separation technique for mixtures with an azeotropic composition or mixtures of components with a relatively small difference in volatility. Besides, a major advantage of pervaporation over the more conventional separation techniques like, e.g. distillation and extraction is the low energy consumption. Pervaporation is especially suitable for the separation of mixtures where the concentration of the component to be removed is less than ± 30 wt.%.

Membrane Transport in Pervaporation

The transport of a component i through a membrane is often described by Fick's law with a concentration gradient as the driving force

$$J_i = -D_i \frac{dc_i}{dz} \tag{1}$$

In the case of non-ideal systems where sorption and diffusion are concentration dependent, transport described by Fick's law becomes more complicated. For a single component i, often an exponential concentration dependency of the diffusion coefficient is used [7,8].

$$D_i = D_{i,0} \exp(A_i . c_i) \tag{2}$$

where $D_{i,0}$ is the diffusion coefficient of component i at concentration zero, A_i is a plasticizing coefficient expressing the increase of polymer chain mobility due to sorption of component i, and c_i is the concentration of component i in the membrane.

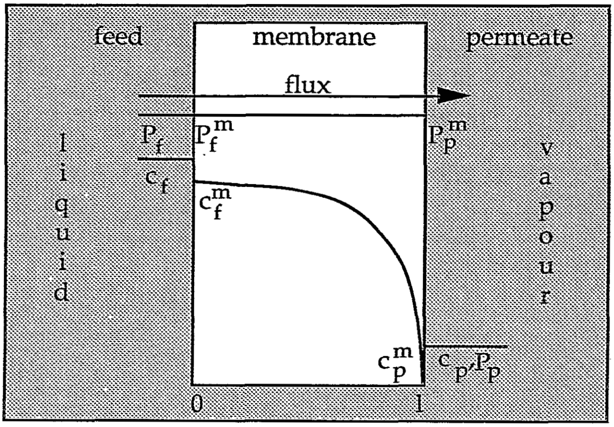


Figure 5 *Concentration and pressure profile for a single component in a pervaporation membrane*

The concentration and pressure profiles in the membrane for a single component are schematically represented in figure 5.

In the case of a binary mixture two components are absorbed in the membrane and both have an influence on the mobility of the polymer chains as well as on the mobility of the other component. The diffusion coefficients of components i and j of a binary mixture in a membrane can be given by the exponential relations

$$D_i = D_{i,0} \exp(A_{ii}c_i + A_{ij}c_j) \tag{3a}$$

$$D_j = D_{j,0} \exp(A_{ji}c_i + A_{jj}c_j) \tag{3b}$$

The plasticizing coefficients, A_{ii}, A_{jj}, A_{ij} and A_{ji} can not be determined experimentally and have a large influence on the curvature of the concentration profile in the membrane [7]. Models based on Fick's law have been developed e.g. by Greenlaw et al. [9,10] and Brun et al. [11].

A better transport description is given by a relation where the driving force is expressed as a gradient of the chemical potential. According to the solution-diffusion model the flux of component i can be described as a product of *concentration, mobility* and *driving force*

$$J_i = -c_i\, m_i \frac{d\mu_i}{dz} \tag{4}$$

with

$$m_i = \frac{D_{i,T}}{RT} \tag{5}$$

The concentration, mobility and driving force will be discussed in more detail in the following part.

Concentration

The concentration in the membrane is not constant over the entire membrane thickness and decreases in the direction of diffusion (see figure 5). It is assumed that at the interphases thermodynamic equilibrium exists, i.e. the chemical potential of component i in the membrane at the feed side will be equal to the chemical potential of component i in the feed [12]. This means that the concentration of component i in the membrane at the feed side can be determined by equilibrium sorption experiments. The concentration at the permeate side is almost zero in the case the permeate pressure is low, because desorption is a rather fast process.

Interfacial concentrations lower than the equilibrium sorption value will be obtained during pervaporation in the case diffusion is faster than sorption resulting in a (liquid) boundary resistance [12,13], e.g. concentration polarization. The boundary resistance increases relatively when the membrane thickness decreases [12,13]. Concentration polarization typically takes place in systems where the concentration of one of the components present in the feed is very small and the membrane is highly selective for that component [14].

Mobility

The mobility as expressed by relation (5) contains the thermodynamic diffusion coefficient $D_{i,T}$. The thermodynamic diffusion coefficient is related to Fick's diffusion coefficient by the relation

$$D_i = D_{i,T} \frac{\ln a_i}{\ln c_i} \tag{6}$$

Driving Force

For isothermal processes the chemical potential is a function of the activity and pressure. For a component i the chemical potential is given by

$$\mu_i = \mu_{i,0} + RT\ln a_i + V_i(P_i - P_{ref}) \tag{7}$$

The driving force across the membrane becomes

$$\frac{d\mu_i}{dz} = RT\frac{d(\ln a_i)}{dz} + V_i\frac{dP_i}{dz} \tag{8}$$

The pressure difference between the feed side and the permeate side is normally about 1 bar in pervaporation processes. With pressure differences of this magnitude the pressure term in relation (8) can be neglected ($V_i \approx$

10^{-4} m^3/mol, $\Delta p_i \approx 10^5$ N/m^2 and RT≈ 2500 J/mol from which it follows that $RT\Delta \ln a_i >> V_i \Delta p_i$). The driving force can than be expressed by

$$\frac{d\mu_i}{dz} = RT\frac{d(\ln a_i)}{dz} \tag{9}$$

Flux

The component flux for a binary mixture can now be expressed as

$$J_i = -c_i\, D_{i,T}\frac{d(\ln a_i)}{dz} \tag{10}$$

This relation has been used by several authors [7, 8, 15] as a starting point for modelling transport through homogeneous membranes.

Selectivity

In case of binary liquid mixtures equation (10) can be used for both components separately. The ratio of the component fluxes per unit of the feed concentration is a measure for the selectivity and can therefore be defined by

$$\alpha(i/j) = \frac{(J_i/x_i)}{(J_j/x_j)} \tag{11}$$

Temperature

By increasing the feed temperature the flux normally increases exponentially, according to an Arrhenius type of relationship

$$J_i(T) = Ar.\exp(\frac{-\Delta E_{pv}}{RT}) \tag{12}$$

The activation energy for pervaporation, ΔE_{pv}, consists of the molar sorption enthalpy and the diffusion energy. For both components diffusion will increase with temperature, but it does not automatically mean that the selectivity remains constant; the activation energy is generally not the same for both components.

DEHYDRATION OF ACETIC ACID BY PERVAPORATION

Economics

In the framework of a BRITE-project "dehydration of organic acids by pervaporation" (nr. RI1B-196) BP Chemicals, one of the partners is studying the economics of drying acetic acid, either by using pervaporation or by distillation [16]. Two cases were investigated: the equipment and utility costs for pervaporation and distillation are either calculated as a function of the flow rate or as a function of the feed concentration.

For pervaporation the feed was introduced at a temperature of 100 °C and at a pressure of 4 bar. In the case of distillation the feed temperature was 120 °C and the pressure was 1.3 bar. In the calculations the membrane costs were estimated on £700/m^2 (which comprises condensers, pumps and instrumentation) for units of at least 500 m^2 membrane area.

A distinction has been made between the equipment costs and the utility costs. For pervaporation the equipment costs consist of membrane costs and installation costs and the equipment costs for distillation consist of the total fixed capital costs (which comprises all equipment costs, design contingency, indirect costs and offsites).

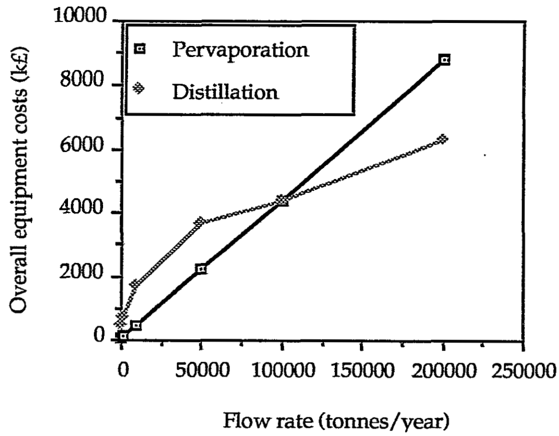


Figure 6 *Economics of pervaporation and distillation for the dehydration of acetic acid; the overall equipment costs are given as a function of the flow rate; product composition: 99.86 wt.% acetic acid*

The utility costs in both cases consist of the costs for steam, cooling water and electricity. The results of this study are summarized in the figures 6-9.

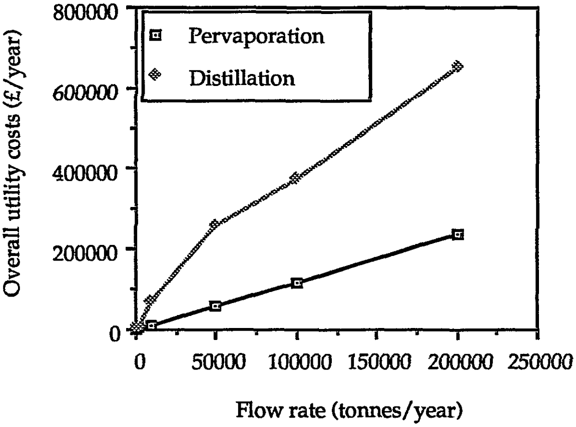


Figure 7 *Economics of pervaporation and distillation for the dehydration of acetic acid; the overall utility costs are given as a function of the flow rate; product composition: 99.86 wt.% acetic acid*

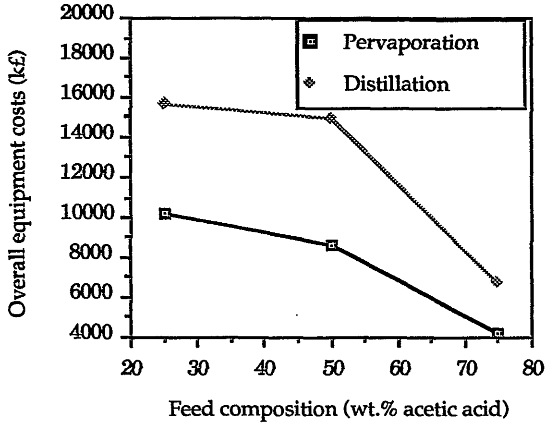


Figure 8 *Economics of pervaporation and distillation for the dehydration of acetic acid; the overall equipment costs are given as a function of the feed composition (flow rate: 200.000 tonnes/year); product composition: 90 wt.% acetic acid*

A feed composition of 95 wt.% acetic acid and 5 wt.% water was used for the calculations in pervaporation as well as in distillation as represented in figures 6 and 7. The permeate/column head contains 5 wt.% acetic acid except in the case of pervaporation at a flow rate of 100 and 1000 tonnes/year where the permeate composition was 25 wt.% acetic acid. The product composition in both processes was 99.86 wt.% acetic acid and for pervaporation a flux of 0.167 kg/m^2h was used in the calculations.

In figure 8 ad 9 the flow rate in all cases is 200,000 tonnes/year, the permeate /column head contains 2 wt.% acetic acid, and the product composition in both processes is 90 wt.% acetic acid.

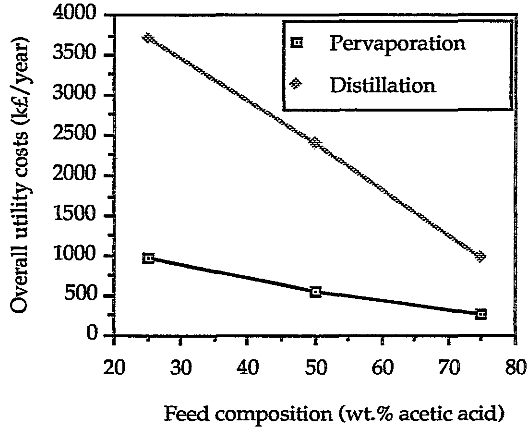


Figure 9 *Economics of pervaporation and distillation for the dehydration of acetic acid; the overall utility costs are given as a function of the feed composition (flow rate: 200.000 tonnes/year); product composition: 90 wt.% acetic acid*

From figures 6 and 7 it can be concluded that for the dehydration of 95 wt.% acetic acid pervaporation is always cheaper than distillation for flow rates smaller than 100,000 tonnes/year.

From figures 8 and 9 it can be concluded that for a flow rate of 200,000 tonnes/year pervaporation is advantageous for the entire feed composition range and this process appears to be especially interesting for the purpose of concentrating solutions from 25 - 50 wt.% to end values of 80-90 wt.% acetic acid. This study shows that pervaporation can be a good alternative for distillation, especially at relatively low flow rates.

Research Survey

Until recently, research in pervaporation was mainly focussed on the dehydration of ethanol. Since a few years also other systems are studied as well.

The first publication on the dehydration of acetic acid is a patent from Kirkland et al. [17] published in 1965. They used modified and crosslinked copolymers of vinyl chloride and vinyl acetate. The best selectivity they claimed was $\alpha = 13.6$ using a feed of 67 wt.% acetic acid at a temperature of 140 °C.

Yoshikawa et al. [18] studied the separation properties for the entire acetic acid/water feed composition of two copolymers, viz. polyacrylicacid-co-acrylonitrile and polystyrene-co-acrylonitrile. These membranes show rather low fluxes.

Nguyen et al. [19] investigated blends of polyvinylalcohol (PVA) and polyacrylicacid (PAA), poly(N-vinyl-2-pyrrolidone) (PVP), polyethyleneimine (PEI) and polyhydroxycarboxylate (PHC) with respect to their dehydrating ability of acetic acid. A feed of 90 wt.% acetic acid at a temperature of 25 °C was used. All PVA blends resulted in poorly selective membranes, unsuitable for dehydration.

Huang et al. studied the properties for acetic acid/water separation of membranes prepared from crosslinked PAA and nylon-6 blends [20,21,22] as well as PVA crosslinked with amic acid [23,24,25]. The effect of the feed composition on the selectivity as well as the influence of the feed temperature were investigated. By increasing the content of PAA in the blend the flux increased, while the selectivity decreased. The crosslinked PVA membrane showed a higher selectivity than the PVA membrane measured by Nguyen et al.[19].

Maeda at al. [26] studied aromatic glassy polymers which have no hydrophilic groups like SO_3, COOH, OH, etc. in the polymer chain. The membranes have been measured at a temperature of 70 °C using a feed of 80 wt.% acetic acid. The membranes of the polymers used by Maeda showed extremely high selectivities.

Cation and anion exchange membranes have been investigated by Böddeker et al. [27,28]. Among others the commercial membranes: Nafion, Selemion and Neosepta were studied. The complete composition range was studied at a temperature of 60 °C. However, these membranes showed rather low selectivities for the dehydration of 80 wt.% acetic acid.

A complete survey of the literature results are represented in tables 1 and 2.

Table 1 *Selectivity and flux of polymer membranes for the dehydration of acetic acid by pervaporation*

Polymer	feed (wt.% acid)	selectivity	flux (kg/m^{2}h)	d (µm)	T (°C)	lit.ref
PVC-*co*-PVAc	67	13.6	-	20	140	[17]
PAA-*co*-PS	90	41	0.0005	17	15	[18]
PAA-*co*-PAN	80	180	0.0025	18	15	[18]
Nylon-6/PAA	75.5	69.5	0.043	?	15	[20-22]
PVA	90	7.4	0.50	30	25	[19]
PVA/PVP*	90	2.8	0.80	30	25	[19]
PVA/PEI*	90	2.0	1.40	30	25	[19]
PVA/PAA*	90	17.5	0.30	30	25	[19]
PVA/PHC*	90	33.8	0.140	30	25	[19]
PVA	90	20.5	0.420	40	75	[23-25]
PSF	80	450	0.63	1**	70	[26]
PES	80	810	0.84	1	70	[26]
PI 2080	80	5500	0.33	1	70	[26]
PPA	80	300	0.46	1	70	[26]
PPO	80	260	0.62	1	70	[26]
PC	80	260	0.43	1	70	[26]
PAI	80	800	0.44	1	70	[26]

PVC=poly(vinyl chloride); PVAc=poly(vinyl acetate); PAA=poly(acrylic acid); PS=polystyrene; PAN=polyacrylonitrile; PVA=poly(vinyl alcohol); PVP=poly(N-vinyl-2-pyrrolidone); PEI=polyethyleneimine; PHC=polyhydroxycarboxylate, PSF= polysulfone; PES=polyethersulfone; PI=polyimide; PPA=poly(parabanic acid); PPO=polyphenyleneoxide; PC=polycarbonate; PAI=poly(amide-imide).

* Blend ratio 1:1

** Not real thickness, normalized to 1 µm

Besides data for the sulfonated polysulfone (PSF(SO_3)) membrane, which is not a commercial membrane, table 2 contains the separation properties of commercially available ion exchange membranes for the dehydration of acetic acid.

Table 2 *Selectivity and flux of ion exchange membranes for the dehydration of acetic acid by pervaporation*

Polymer	feed (wt.% acid)	selectivity	flux (kg/m^2h)	T (°C)	lit.ref
Neosepta CM-1	80	10	0.44	40	[28]
Neosepta CM-2	80	11.5	0.22	40	[28]
Selemion AMV	80	4.5	0.83	80	[27]
Selemion CMV	80	4	0.33	80	[27]
Nafion 324	80	4	1.70	80	[27]
PSF(SO_3)	90	9.4	0.016 -	--	[19]

Neosepta CM-1/CM-2 = cation exchange membranes from Tokuyama Soda
Selemion AMV = polytetrafluoroethylene-NH_3^+ from Asahi Chemical
Selemion CMV = polytetrafluoroethylene-COO^- from Asahi Chemical
Nafion = polytetrafluoroethylene-SO_3^- from Du Pont

REMOVING ACETIC ACID FROM AQUEOUS WASTE STREAMS BY MEMBRANE SEPARATION

If water is contaminated with acetic acid (≤ 20 wt.%) two membrane processes can be considered for purification, viz. pervaporation and reverse osmosis.

Pervaporation

In the case of pervaporation a membrane material has to be found which is preferentially permeable for acetic acid. In general, elastomers are preferentially permeable for organic components. Due to relatively flexible polymer chains selectivity of elastomers is mainly determined by preferential sorption rather than by preferential diffusion. Since, both water and acetic acid contain polar groups with hydrogen bonding ability a material which preferentially absorbs acetic acid will be difficult to find.

Reverse Osmosis

Reverse osmosis is a membrane separation process specially developed for the desalination of sea and brackish water. Due to a pressure gradient across the membrane water will pass the membrane while salt is rejected.

Nowadays reverse osmosis is also used for the purification of ground and drinking water, contaminated with organic solutes. The concentration of these solutes can not be too high ($\leq$ 15 wt.%) otherwise too much energy will be needed to overcome the osmotic pressure.

In reverse osmosis the selectivity is mostly expressed by the rejection coefficient R, defined as

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\ \% \qquad (13)$$

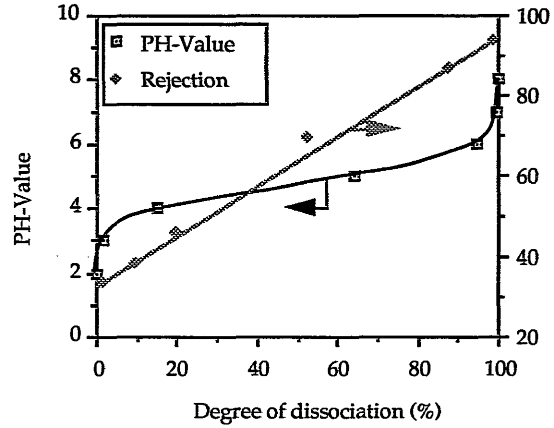


Figure 10 *Rejection and PH-value of acetic acid in water as a function of the degree of dissociation; NS-100 membrane; 0.01 M acetic acid [29]*

For solutes which can dissociate, like the aliphatic acids, the rejection appears to be dependent on the degree of dissociation; the solute rejection increases proportionally with the degree of dissociation (as shown in figure 10) and decreases with increasing dissociation constant [29,30].

The separation properties of the reverse osmosis membranes are generally related to salt solutions, but a reverse osmosis membrane with a higher salt rejection will also exhibit a higher rejection for organic dissociated solutes. The rejection and flux normally increase with increasing feed pressure and with decreasing feed concentration.

In table 3 some commercially available reverse osmosis membranes are given showing the characteristics for the system water/acetic acid.

Table 3 *Rejection and flux of some commercial reverse osmosis membranes for the separation of a solution of 10 wt.% acetic acid in water [31]*

Membrane	Rejection (%)	Flux (kg/m^{2}day)
CA	6.24	565
PA-300	32.4	548
PA-100	46.2	462
RC-100	58.8	126
NS-200	64.0	152
FT-30	64.1	214
NS-100	68.5	95
PEC-1000	84.0	141

Operating conditions: 56 kg/cm^2, 25 °C

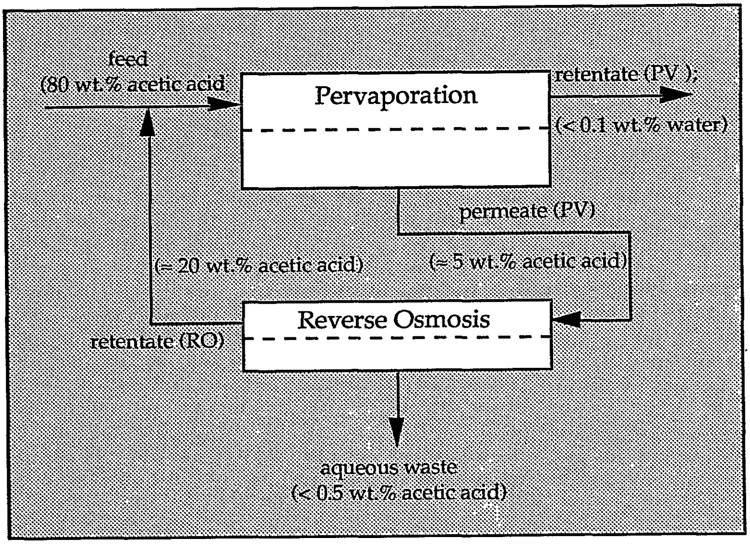


Figure 11 *A combination of pervaporation and reverse osmosis for the*

dehydration of 80 wt.% acetic acid

Since environmental laws become more and more stringent with respect to the concentration of organics in waste water streams to be discharged, reverse osmosis becomes a useful separation process for the after-treatment of the permeate stream in the dehydration process of organics by pervaporation, like e.g. acetic acid. A schematic representation of such a hybrid system for the dehydration of 80 wt.% acetic acid is given in figure 11.

STRUCTURE OF THIS THESIS

In this thesis the material science aspects for developing acetic acid resistant membranes suitable for the dehydration of acetic acid at elevated temperatures are emphasized.

At first, in chapter 2 the chemical stability of commercially available polymers in acetic acid at elevated temperatures is studied. Then, polymers that show an acceptable resistance were tested in a pervaporation set-up, using a feed of 80 wt.% acetic acid in water at 80 °C. The polymers with relatively high selectivities have been investigated more extensively with respect to i) long term chemical stability, ii) sorption selectivity, and iii) polymer modification by chemical reaction; the chemical modification of polyether-ether-ketone and polysulfone is described in appendix A (following chapter 5).

One way to increase membrane flux is to decrease the effective membrane thickness. This can be accomplished by developing an integrally skinned asymmetric membrane. The development of such a membrane in the configuration of a hollow fiber and made of polysulfone is described in chapter 3. A spinning process using two different nonsolvents as a coagulant for the polymer spinning dope is used (dual-bath method). All kinds of spinning parameters like i) first coagulant, ii) solvent of the polymer, iii) polymer concentration, iv) additive concentration in the spinning dope, and v) bore liquid composition have been investigated. High flux membranes could be obtained, but the intrinsic selectivity as determined in chapter 2 could never be reached. In the appendix of chapter 3 possible resistances in the support layer and at the bore side of the hollow fibers are discussed.

In chapter 4 the selectivity and flux of relatively thick and thin membranes are compared for the processes of pervaporation (dehydration of acetic acid) and gas separation (separation of CO_2 and CH_4). Models based on the solution-diffusion model describe permeability in gas separation as well as in pervaporation as being proportional to the reciprocal membrane thickness. Since this relation is valid for both components the selectivity should be independent on membrane thickness. Experimentally deviations from the theoretical selectivity values are found in pervaporation in the case of thin dense films. Possible explanations for this phenomenon are discussed.

The development of a composite membrane consisting of a polyvinylchloride (PVC) toplayer supported by a porous polyacrylonitrile (PAN) sublayer is described in chapter 5. Also the influence of the support layer on the selectivity as well as the separation properties of dense bi-layer membranes of PVC and PAN are described.

LIST OF SYMBOLS

		unity
a	= activity	
A	= plasticizing constant	
Ar	= Arrhenius constant	$kmol/m^2s$
α	= selectivity	
c	= molar concentration	$kmol/m^3$
D	= Fick's diffusion coefficient	m^2/s
D_T	= Thermodynamic diffusion coefficient	m^2/s
ΔE	= activation energy	kJ/kmol
J	= molar flux	$kmol/m^2s$
l	= membrane thickness	m
P	= pressure	bar
R	= gas constant	J/mol K
T	= temperature	K
μ	= chemical potential	J/mol
μ_0	= standard chemical potential	J/mol
V	= molar volume	m^3
x	= molar fraction (liquid phase)	
y	= molar fraction (vapour phase)	
z	= distance in membrane	m

indices

f = feed side
i = component i
j = component j
m = membrane
p = permeate side
pv = pervaporation
ref = reference

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2

MATERIAL SELECTION FOR THE DEHYDRATION OF ACETIC ACID BY PERVAPORATION

INTRODUCTION

During the synthesis of acetic acid often water is produced, which has to be removed in order to fulfil the product standards of glacial acetic acid. In addition, in the production of vinyl acetate, cellulose acetate, terephthalic acid and acetate esters, acetic acid is used as a basic material. In these processes aqueous acetic acid streams are generated as a by-product, from which the acetic acid has to be recovered.

Distillation and liquid-liquid extraction are still the most commonly used techniques for these separations. However, due to the high energy consumption and the increasing energy prices less energy consuming processes become interesting. One of these alternative processes is pervaporation, a membrane process which separates liquid components due to a difference of sorption in and diffusion through a nonporous membrane.

For the dehydration of acetic acid BP Chemicals [1] studied the economics of distillation and pervaporation and showed that pervaporation is cheaper for flow rates smaller than 100,000 tonnes/year. A recent study by SRI International [2] showed that 3.2 trillion KJ/year of energy could be saved for the dehydration of acetic acid when membranes are used in combination with conventional separation techniques.

These studies clearly indicate that pervaporation is an interesting separation process for the dehydration of acetic acid. Nevertheless, highly selective membranes with high fluxes are required for this separation process to be of economical interest. Target values of selectivity and flux at two different feed concentrations are given in table 1.

Table 1 *Target values of selectivity and flux for the dehydration of acetic acid by pervaporation*

Feed (wt.% acid)	permeate (wt.% acid)	selectivity	Flux (kg/m^{2}h)
80	≤ 2	≥ 196	≥ 0.5
98	≤ 20	≥ 196	≥ 0.2

The intrinsic selectivity is a material property and can only be influenced by chemical modification of the membrane. On the contrary, the membrane flux cannot only be influenced by chemical modification, but can also be improved by making the effective separation layer thinner; the flux is inversely proportional to the effective membrane thickness.

Besides having the required separation properties the membrane material has to be *chemically* stable in the liquid feed mixture under pervaporation conditions. Typical feed compositions that can be considered for the dehydration process consist of 80 wt.% acetic acid or more, which means that the membrane material has to be chemically resistant towards concentrated acetic acid. In addition, these separations are practically always carried out at elevated temperatures, up to 80-90 °C, which requires even more of the stability of the membrane material.

In addition, the *mechanical* stability of the membrane material is also important and should not be underestimated. The loss in mechanical stability by making the separating layers as thin as possible can be overcome by laminating these layers on a porous support, but the sensibility for environmental stress-cracking of amorphous polymers, like e.g. polysulfone and polyethersulfone [3] due to sorption of organic solvents cannot always be avoided.

In order to find a membrane material suitable for the dehydration of acetic acid glassy polymers should be selected that are highly water selective. At this stage of membrane material selection flux is not so important. Once a material has been selected, an optimum flux can be obtained by developing a membrane with a separating layer as thin as possible, either by developing a composite membrane or by producing an asymmetric integrally skinned membrane.

Chemical Stability

Many polymers show at least some degradation in acidic solutions. This degradation phenomenon will be enhanced at elevated temperature and increasing acid concentration.

In the presence of water dehydration catalysed by the hydronium ion, H_3O^+, is often responsible for polymer degradation. Reaction catalysis by H_3O^+ is known as *specific acid catalysis*. The rate of polymer degradation can be expressed by

$$r = k_H [H_3O^+][\text{polymer}] \tag{1}$$

where k_H is the catalytic constant of H_3O^+.

In acidic solutions H_3O^+ is not always the only species that causes degradation. Catalyses by the acid itself can take place as well, which is known as *general acid catalysis*. The reaction rate can now be expressed by

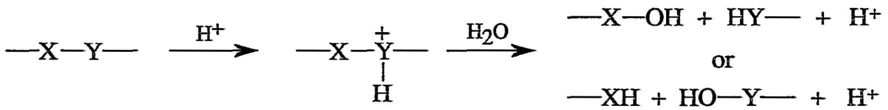
$$r = k_H [H_3O^+][\text{polymer}] + k_z[\text{acid}][\text{polymer}] \tag{2}$$

here k_z is the catalytic constant of the acid.

General acid catalysis becomes only important in dilute acid solutions, where the influence of $[H_3O^+]$ is negligible because of its low concentration. On the other hand the catalytic influence of the acid is negligible at low pH-values, where it will be dominated by the larger contribution of H_3O^+.

Generally, polymers with heteroatoms in the main chain or in side chains are sensitive towards degradation in acidic solutions. On the other hand, polymers with a carbon chain backbone without double bonds and without heteroatoms in the side chains are highly chemical resistant, like e.g. polyethylene and polypropylene.

Unstable bonds mostly decompose in acid media as a result of acid catalysed hydrolysis. A common acid catalysed degradation mechanism can be written as



$$—X—Y— \xrightarrow{H^+} —X—\underset{\overset{|}{H}}{\overset{+}{Y}}— \xrightarrow{H_2O} \begin{array}{c} —X—OH + HY— + H^+ \\ \text{or} \\ —XH + HO—Y— + H^+ \end{array}$$

Degradation according to this mechanism takes place for the following polymers:

polymers	X is:	Y is:
amides, imides	C=O	N
urethanes	O-C=O	N
carbonates	O-C=O	O
esters	C=O	O
siloxanes	O	Si
ethers, acetals(polyoxymethylene, cellulose)	C	O

The chemical stability of commonly used types of polymers in acid media will be discussed in more detail in the appendix of this chapter.

A disadvantage of chemical resistant polymers is their poor solubility and processability. This makes it difficult or even impossible to prepare membranes by solution casting. The choice of acetic acid resistant polymers for membrane development therefore is restricted. Membranes can sometimes be made by extrusion, followed by a calendering process and stretching of the polymer. However, this method cannot be used for the preparation of composite membranes consisting of an ultra thin film on top of a porous support.

A summary of the chemical resistance in concentrated acetic acid of several polymers as found in literature is represented in table 2.

Table 2 *Chemical resistance in concentrated acetic acid at room temperature of several polymers*

Polymer	resistance in concentrated acetic acid	reference
PET	-	[4]
PC (bisphenol-A)	-	[5]
Nylon-6	-	[6]
Nylon-6,6	-	[6]
Nylon-6,10	-	[6]
Nylon-11	-	[6]
PE	+	[7]
PP (iso-tactic)	+	[7]
PMMA	-	[8]
PMMA-*co*-PAN	-	[8]
PSF	+	[3]
PES	+	[3]
PEEK	+	[9]
PVDF	+	[9]
PTFE	+	[9]
PVF	+	[10]
PVC	-	[9]
PPS	+	[11]
PVA	-	[12]
PI	-	[12]
PPO	+/-	[12]

Except for PE, PP, PTFE and PPS all polymers showing good resistance towards concentrated acetic acid according to literature are studied in this chapter. From the polymers showing a poor resistance only high molecular weight PVC and two different polyimides were studied.

EXPERIMENTAL

materials

Polyacrylicacid (PAA) was obtained from Aldrich, polyacrylonitrile (PAN-7A) from Du Pont, polyacrylonitrile-co-maleicanhydride (PAN-MA) from Polyscience, polydimethylsiloxane (PDMS, RTV 615 A+B) from General Electric, polyether-ether-ketone (PEEK, Stabar K 200 film) from ICI, polyetherimide (PEI, Ultem 1000) from General Electric, polyethersulfone (PES, Victrex 4800p) from ICI, polyethylene-*co*-vinyl alcohol (EVOH, Clarene) from Solvay, polyimide (PI, Upilex S film) from ICI, polyimide (PI 2080) from Lenzing AG, polyoxy-3,5-dimethylphenylene (PPO) from General Electric, polysulfone (PSF, Udel P3500) from Amoco, polyvinylchloride (PVC, high Mw) from Aldrich, carboxylated (1.8 %) polyvinylchloride (PVCcarb) from Aldrich, polyvinylidenefluoride (PVDF, Solef 2008) from Solvay, and polyvinylfluoride (PVF, Tedlar film) from Du Pont.

The solvents used were of analytical grade and obtained from Aldrich.

Membrane Preparation

The polymers were dissolved in a suitable solvent, casted on a glass plate and put into a nitrogen atmosphere where the solvent was evaporated at room temperature. After the solvent had evaporated (after ± 12 hours) the membrane was removed from the glass plate and dried in a vacuum oven at 80 °C or 150 °C, dependent on its thermal stability, in order to remove the residual solvent. The membranes used for the chemical stability experiments had a thickness of about 50-80 μm and were dried until constant weight. The membranes used for pervaporation experiments had a typical thickness of 20-30 μm and were dried for 1 week.

Chemical Stability

Pieces of polymer films with a weight varying between 0.4 and 0.6 grams were dried until constant weight before they were immersed into a 90 wt.% or 99 wt.% acetic acid solution at 80 °C for a certain period of time. After that time the film was removed from the acid solution and dried for 5 days or even longer until a constant weight was obtained again. The difference in weight before and after being in contact with the acetic acid solution gives an indication of the stability of the polymer in concentrated acetic acid at elevated temperatures.

In case weight changes are measured in time after the first contact period, the same polymer sample was immersed again in the acetic acid solution for a second period of time, etc.

Chain cleavage of the polymers was measured by determination of the weight average molecular weight of the samples before and after being in contact with acetic acid using a Gel Permeation Chromatography (GPC) technique. The polymers studied were dissolved (0.5 wt.%) in N,N-dimethylformamide (DMF), except for PVC which was dissolved in tetrahydrofuran (THF). The weight average molecular weight of all polymers was related to the molecular weight of polystyrene in THF. To separate the high molecular weight fraction from the lower molecular weight fraction 4 different micro-styragel columns were used with the following pore sizes: 10^6, 10^5, 10^4 and 10^3 Å.

Pervaporation

Pervaporation experiments were carried out using a set-up schematically represented in figure 1. The set-up was totally made of glass. The permeate side was maintained at a pressure of 0.1-0.5 mmHg by a Crompton Parkinson vacuum pump. The pressure was measured by an Edwards pirani meter. Samples of the permeate were taken every hour, during 8 hours. Steady state was normally obtained after 3 to 4 hours. The permeate was analysed using a Varian 3700 Gas Chromatograph filled with a Poropack Q column at a temperature of 190 °C.

Sorption and Sorption Selectivity

Sorption experiments were carried out with polymer samples of a dry weight varying between 0.4 and 0.6 grams. After drying under vacuum at 80 °C till a constant weight was obtained the polymer samples were immersed into mixtures with various concentrations of acetic acid and water as well as in the pure liquids at 80 °C. After 7 days of immersion the mass uptake was determined by measuring the weight of the swollen polymer sample. Before weighing, the sample was removed from the acetic acid/water mixture, dried between tissue paper and put into a petri dish. After waiting for 15 minutes to cool down the samples to room temperature the samples were weighed. The mass uptake in grams per 100 gram of dry material represents the degree of sorption (%).

The sorption selectivity was determined by measuring the acetic acid and water content in the membrane film independently. Therefore, the swollen sample was divided into two parts. One piece was dissolved in tetrahydrofuran (THF) or in N,N-dimethylformamide (DMF) and the acetic acid concentration was determined by titration with tert-methyl-ammoniumhydroxide. The other piece was used for the determination of the water content. The water content was determined by a Carl-Fisher reaction after it was distilled out of the polymer sample.

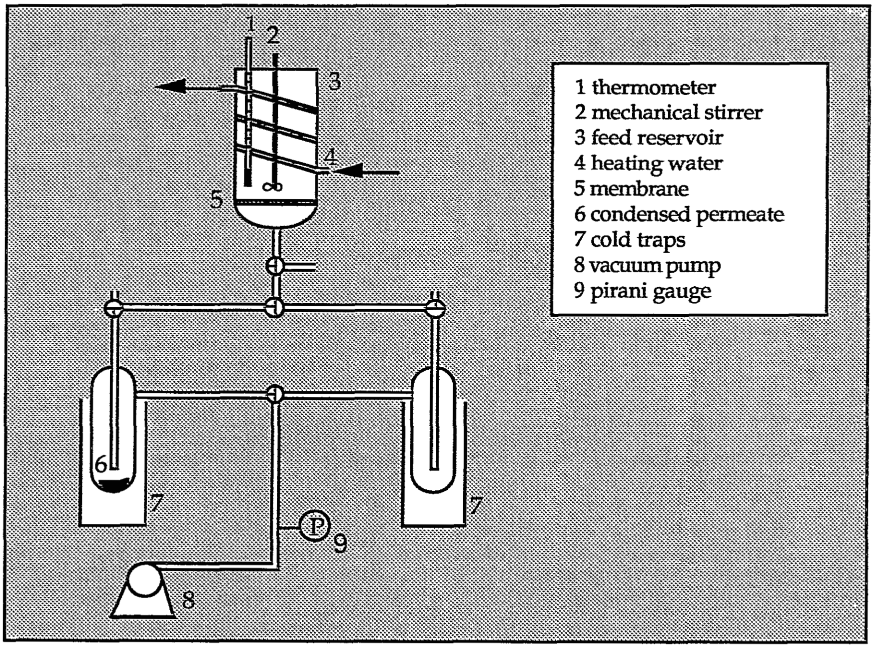


Figure 1 *Schematic representation of the pervaporation set-up*

RESULTS AND DISCUSSION

Chemical Stability I

The selection of polymers that are suitable to be used as a membrane material for the dehydration of acetic acid can be carried out using two different approaches. Firstly, materials that are highly selective for the dehydration of a standard acetic acid mixture will be selected, followed by a study of the chemical and thermal stability of that material. A second approach is the other way around, acetic acid resistant materials will be selected followed by pervaporation experiments to measure their dehydration ability.

Although, not all polymers have been tested for their resistance towards concentrated acetic acid, a first rough selection could be made from information found in literature (see table 2). Therefore, the latter approach seems to be less time consuming. Pervaporation instead of sorption is chosen because it gives more direct information with respect to selectivity and flux.

Several polymers were measured for their resistance in 90 wt.% acetic acid at 80 °C for 48 hours by measuring the change in weight of the polymer sample. The weight change is defined as

$$\Delta m = \frac{(m_0 - m_t)}{m_0} \times 100\% \qquad (3)$$

with

m_0 : sample weight before immersion
m_t : sample weight after immersion and drying

The results of these experiments are represented in table 3. From this table it can be concluded that PSF, PEEK, PI Upilex S, and also PES and PVC show a high resistance in 90 wt.% acetic acid. PI Upilex S is probably a crosslinked polyimide because the polymer film appeared to be insoluble. This also explains the chemical resistance of PI Upilex S in acetic acid.

The purple color of PVC implies degradation by dehydrochlorination [13] however, no influence on selectivity and flux could be observed, as will be discussed in the second paragraph about chemical stability. PVDF, PAN and PVF show a weight increase, which can be caused by chemical reaction with the acetic acid or by the fact that the polymer samples still contained some of the absorbed liquid.

The stability of PPO, PAN-MA and PEI with a weight decrease between 1% and 2.5% is not good enough. PI 2080 with a weight decrease of more than 5% is absolutely not resistant towards 90 wt.% acetic acid.

Table 3 *Weight change of several polymers after being in contact with 90 wt.% acetic acid at 80 °C for 48 hours*

Polymer	Δm (wt.%)	remarks
PSF	- 0.067 ± 0.025	
PES	- 0.62 ± 0.21	
PEEK	0.0	
PVDF	+ 0.467 ± 0.006	
PPO	- 1.42 ± 0.25	
PAN	+ 1.10 ± 0.04	
PAN-MA	- 2.14 ± 0.09	
PVC	- 0.94 ± 0.05	becomes purple
PVF	+ 0.9	
PI-Upilex S	0.0	
PI 2080	- 5.09 ± 0.08	
PEI	- 1.14 ± 0.10	becomes white, opaque

This type of experiment gives a first impression of the chemical resistance of the polymers in acetic acid. To decide whether it is useful to study the chemical resistance in more detail pervaporation experiments were carried out first in order to distinguish between highly water selective materials and less water selective materials.

Pervaporation I

The polymers that showed satisfactory resistance in 90 wt.% acetic acid at 80 °C for 48 hours were studied for the dehydration of a 80/20 wt.% acetic acid/water mixture by pervaporation at 80 °C. The results of these measurements are represented in table 4.

Most of the polymer membranes have been measured several times and the best results are represented in this table; generally, the average value is somewhat lower. Of the 13 measured polymer membranes seven showed relatively high selectivities, with less than 1.5 wt.% acetic acid in the permeate. Extremely low in selectivity are PVDF, EVA and PDMS; the latter is even acetic acid selective.

Table 4 *Selectivity and flux of various acetic acid resistant membranes for the dehydration of 80 wt.% acetic acid at 80 °C by pervaporation*

Membrane	feed. (wt.% acid)	permeate (wt.% acid)	selectivity	flux* (kg/m^2h)
PVC	79.20	0.08	4756	0.019
PAN-MA	79.70	0.10	3922	0.048
PAN	78.20	0.16	2238	0.040
PEEK	79.40	0.18	2137	0.026
PI-Upilex S	80.10	0.63	635	0.010
PSF	80.30	0.65	623	0.037
PES	79.70	1.50	258	0.044
PVCcarb.	79.10	2.20	168	0.034
PPO	79.80	4.00	95	0.103
PVF	81.00	17.40	20	0.064
PVDF	80.30	51.60	4	0.277
EVA**	77.10	70.20	1.4	2.730
PDMS	77.80	83.60	0.7	5.605

* the fluxes are normalized to a membrane thickness of 20 μm

** crosslinked by addition of 4 wt.% dicumylperoxide and heat treated at 175 °C for 17 minutes.

Furthermore, it should be noted that PSF and PES membranes are very hard to measure properly due to solvent induced stress-cracking, which results in leakage of the membranes at the edge where the O-ring is pressed on the membranes. Annealing of the membranes at 200 °C for 1 hour reduces sensitivity for solvent induced stress-cracking and made it possible to obtain the results presented in table 4.

According to the high selectivity the following materials seem to be interesting for further investigation: PVC, PAN-MA, PAN, PEEK, PI-Upilex S, PSF and PES. The separation properties of most of these polymers using a feed of 98 wt.% acetic acid are represented in table 5.

PI-Upilex S was not used for further study, because it can only be applied as an extruded, insoluble film. The polymer PAN-MA was not used further because of its doubtful stability in acetic acid (see table 3). Probably, this also explains the relatively low selectivity for the dehydration of 98 wt.% acetic acid at 80 °C.

Table 5 *Selectivity and flux of reasonably to highly acetic acid resistant membranes for the dehydration of 98 wt.% acetic acid at 80 °C by pervaporation*

Membrane	feed. (wt.% acid)	permeate (wt.% acid)	selectivity	flux* (kg/m^2h)
PAN	98.20	16.30	280	0.006
PES	97.90	15.80	248	0.013
PVC	98.00	37.30	82	0.023
PVCcarb.	98.2	64.30	30	0.078
PAN-MA	98.20	86.30	9	0.029

* flux is normalized to a membrane thickness of 20 μm

Table 5 shows that the amount of acetic acid in the permeate for the dehydration of 98 wt.% acetic acid is much higher than in the case of 80 wt.% acetic acid, especially for PVC and PAN-MA. This phenomenon can be explained by the fact that the degree of total sorption, which will be discussed lateron (see table 10), increases with the acetic acid concentration in the feed, together with an increasing driving force for acetic acid permeation.

PSF could not be measured at 98 wt.% acetic acid due to sorption induced stress-cracking of the membrane during pervaporation.

Chemical Stability II

The highly selective materials (see table 4) PSF, PAN, PVC, PEEK and PES have been investigated more intensively with respect to their stability in concentrated acetic acid in time. In table 6 the weight change in 99 wt.% acetic acid at 80 °C as a function of time has been represented. After each period of time the polymer samples (in triplo) were removed from the acetic acid solution, dried under vacuum at 80 °C for 5 days and weighed. After weighing, the same polymer samples were immersed again into the acetic acid solution, etc.

From the experiments it can be concluded that all the investigated polymers, except for PAN, show satisfactory resistance to concentrated acetic acid.

Table 6 *Weight change of PSF, PAN, PVC, PEEK and PES in 99 wt.% acetic acid at 80 °C as a function of time*

Polymer	2 days (wt.%)	9 days (wt.%)	23 days (wt.%)	51 days (wt.%)
PSF	-0.45 ± 0.04	-0.29 ± 0.02	-0.23 ± 0.04	-0.36 ± 0.05
PAN	+5.26 ± 0.72	+4.29 ± 0.63	+4.46 ± 0.71	+4.03 ± 1.30
PES	-0.57 ± 0.03	-0.55 ± 0.07	-0.40 ± 0.06	-0.22 ± 0.08
PVC	-0.65 ± 0.09	-0.68 ± 0.13	-0.32 ± 0.03	-1.24 ± 0.04
PEEK	0.00	0.00	0.00	0.00

Furthermore, it can be concluded that in the case of PSF and PES the ultimate weight decrease after 51 days has already been obtained after 2 days, which can be attributed to dissolution of low molecular weight compounds.

PEEK appears to be the most resistant polymer, but it has the disadvantage that it is only soluble in strong acids like concentrated sulfuric acid, methane sulfuric acid and chlorosulfonic acid [14]. The chemical modification of PEEK in order to improve its solubility is described in appendix A following chapter 5.

The weight decrease of PVC can be partly attributed to dissolution of low molecular weight particles and partly due to dehydrochlorination. If the weight decrease of PVC is totally attributed to dehydrochlorination it can be calculated that this degree is only about 2%, which means 2 HCl groups per 100 repeating units have been eliminated from the main chain.

Table 7 *C:H:N ratio of PAN samples before and after being immersed in 99 wt.% acetic acid at 80 °C for 51 days*

Atom	Theoretical (wt.%)	Before (wt.%)	After (wt.%)
C	67.91	68.31	68.97
H	5.70	6.44	6.52
N	26.39	25.25	24.50

PAN seems to react with acetic acid since an increase in sample weight instead of a weight decrease was observed. The ratio C:H:N of a PAN sample was determined by chemical analysis before and after it has been immersed in a 99 wt.% acetic acid solution. From these data, which are represented in table 7, it can be concluded that the C:H:N ratio was changed and that this can be explained by a chemical reaction of acetic acid with the nitrile group of the polymer.

Assuming a weight increase of 6 % due to reaction with acetic acid, which is in good agreement with the weight increase observed experimentally (see table 6) a ratio of 68.92 % carbon, 6.58 % hydrogen and 24.47 % nitrogen can be calculated. This is in good agreement with the ratio represented in right column in table 7.

Besides removal of low molecular weight compounds cleaved from the polymer chain due to degradation of side-groups another degradation phenomenon can occur, i.e. cleavage of the polymer main chain which does not necessarily result in a weight decrease of a polymer film. As long as the cleaved polymer chains are large enough they will not dissolve in the liquid. Therefore, a weight decrease experiment alone will not give enough information to draw conclusions with respect to the chemical stability of the polymer in acetic acid.

To investigate whether chain cleavage has occurred the average molecular weight Mw has been determined before and after the polymer sample had been in contact with a concentrated acetic acid solution. For the determination of the average molecular weight a Gel Permeation Chromatography (GPC) technique was used. The results of these experiments are represented in table 8.

Table 8 *The influence on the average molecular weight (Mw) of immersion of PSF, PAN, PES and PVC in 99 wt.% acetic acid at 80 °C as a function of time*

Polymer	starting value	1 day	7 days	51 days
PSF	96,600	138,900	181,900	189,657
PAN	353,700	336,507	324,556	539,707
PES	478,100	580,300	547,500	667,348
PVC	144,300	-	146,400	76,408

The starting value represents the molecular weight of the raw material before it has been immersed into acetic acid.

GPC is a technique by which the molecular weight of a polymer is determined in solution. PSF, PES and PAN are determined in N,N,-dimethylformamide and PVC is determined in tetrahydrofuran.

It is remarkable to see that the molecular weight of PSF, PAN and PES has increased after being in contact with acetic acid (a second series of measurements gave similar results as the first measurements). This cannot be explained by dissolution of about 1 wt.% low molecular weight compounds (see table 6).

A chemical reaction of acetic acid with the polymer or association of the polymer in solution are phenomena that normally result in a higher molecular weight. Chemical reaction might explain the molecular weight values of PAN, but certainly cannot explain the molecular weight increase of PSF and PES; no functional groups are present in these polymers to react with the acid. Association can only explain the molecular weight increase if association takes place due to small amounts of acetic acid which are present in the polymer samples that have been immersed, even after drying for more than one week at 80 °C (PAN, PVC) or 150 °C (PES, PSF) under vacuum. The observation that films which had been immersed in acetic acid needed a longer time to dissolve than films which had not been in contact with acetic acid might be an indication for association phenomena. The reason that the increase of the weight average molecular weight was not observed for PVC is probably due to the fact that THF instead of DMF was used as a solvent; THF is a better solvent for PVC than DMF.

Although the molecular weights do not decrease with time, except for PVC, reliable conclusions with respect to degradation of PSF, PES and PAN cannot be drawn from these experiments.

On the other hand PVC shows a clear decrease in molecular weight after being in contact with acetic acid for 51 days; a decrease of almost 50 % could be observed, although the molecular weight was still unchanged after 7 days.

To study the influence on selectivity and flux of a PVC membrane which has been in contact with concentrated acetic acid for a certain period of time a PVC membrane has been immersed in a 98 wt.% acetic acid solution at 80 °C for 14 days. After those 14 days selectivity and flux were measured and compared with a membrane which had not been in contact with acetic acid before. The results of this experiment are represented in

Table 9 *The influence of immersion in concentrated acetic acid on selectivity and flux of a PVC membrane*

Immersion time in 98 wt.% acid (days)	Feed (wt.% acid)	Permeate (wt.% acid)	Selectivity	Flux* (kg/m^{2}h)
0	79.90	0.60	659	0.020
0	97.90	33.00	95	0.021
14	79.90	0.55	719	0.018
14	98.00	35.10	91	0.021

* membrane thickness 13 μm

table 9. From table 9 it can be concluded that selectivity and flux are not influenced at all after the membrane has been in contact with 98 wt.% acetic acid for 14 days.

This experiment together with the weight change experiments (see table 6) showed a rather promising resistance of PVC towards acetic acid, but from the decrease of 50 % of the molecular weight after 51 days one might conclude the opposite. To be absolutely sure about the resistance and the separation behaviour of a PVC membrane with time long-term pervaporation experiments have to be carried out.

Pervaporation II

PVC has a relatively low permeability in comparison to the other highly selective polymers when a feed composition of 80 wt.% acetic acid and 20 wt.% water is used (see table 4). Using 98 wt.% acetic acid and 2 wt.% water as a feed mixture PVC has a relatively high permeability in comparison to the other polymers (see table 5).

To see how selectivity and flux change as a function of the feed composition a PVC membrane has been measured for feed compositions varying from 0-100 wt.% acetic acid at 80 °C. In figure 2 the permeate composition is given as a function of the feed composition, while the component fluxes are given in figure 3.

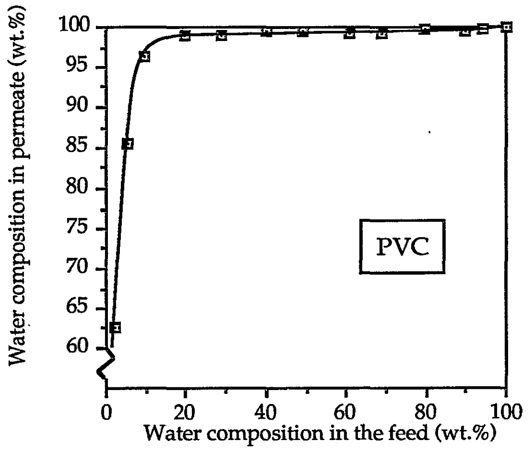


Figure 2 *Permeate composition as a function of the feed composition for the dehydration of acetic acid by pervaporation for a PVC membrane at 80 °C; membrane thickness: 20 μm*

From figure 3 it can be concluded that the water flux is more or less constant in the range of 20-100 wt.% water in the feed mixture.

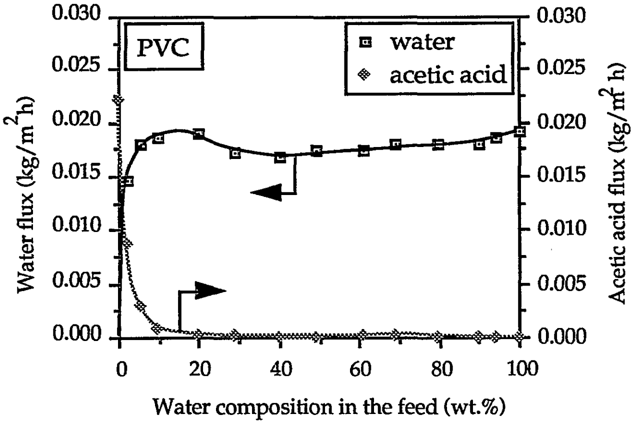


Figure 3 *Water flux and acetic acid flux as a function of the feed composition for the dehydration of acetic acid by pervaporation for a PVC membrane at 80 °C; membrane thickness: 20 μm*

Figure 3 also shows that addition of only a small amount of water to acetic acid results in an enormous decrease of the acetic acid flux and consequently selectivity increases.

The same experiments were carried out with PAN, the polymer with the highest selectivity using a feed of 98 wt.% acetic acid and 2 wt.% water. In figure 4 the permeate composition is given as a function of the feed composition.

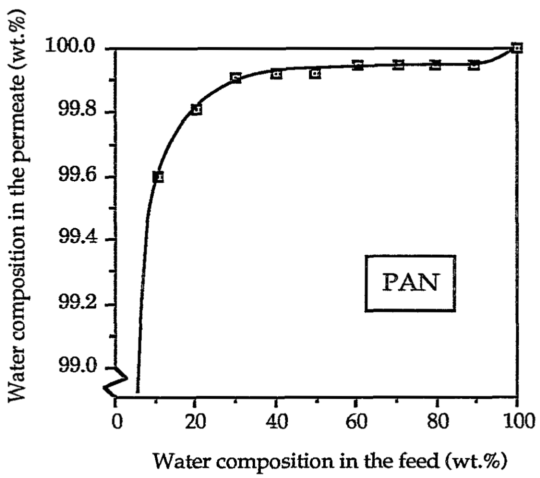


Figure 4 *Permeate composition as a function of the feed composition for the dehydration of acetic acid by pervaporation for a PAN membrane at 80 °C; membrane thickness: 20 μm*

From figures 2 and 4 it can be concluded that PVC and PAN are both highly selective membrane materials for feed compositions of 20-100 % of water and that PAN is more selective for feed compositions of 0-20 % of water.

The water flux and acetic acid flux for PAN as a function of the feed composition are given in figure 5. This figure also shows an enormous drop in acetic acid flux as soon as water is present in the feed. Presumably, the presence of water results in the formation of acetic acid clusters, which reduces the diffusion rate of acetic acid drastically.

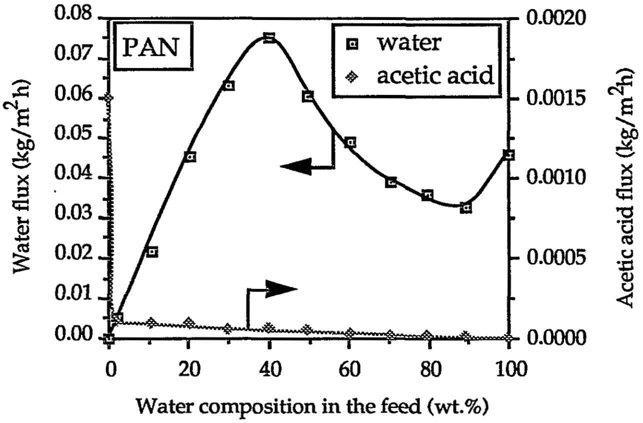


Figure 5 *Water flux and acetic acid flux as a function of the feed composition for the dehydration of acetic acid by pervaporation for a PAN membrane at 80 °C; membrane thickness: 20 μm*

A maximum water flux can be observed at a feed composition of 40 wt.% water. This maximum is more pronounced than in the case of PVC, where a small maximum can be noticed around 15 wt.% water in the feed.

Furthermore, it should be noted that the selectivity of PAN membranes started to decrease after a couple of days, during the measurements where selectivity and flux as a function of the feed composition were studied. This is either due to defects introduced in the membrane by changing the feed or due to a lack of the chemical stability of PAN in acetic acid.

Sorption

Sorption experiments were carried out in mixtures of acetic acid and water, as well as in the pure liquids. The mass uptake was determined after 7 days of immersion. The sorption is defined as the mass uptake per 100 g of dry material. The results of these experiments are represented in table 10.

Except for PAN, all the other polymers show an increase in sorption as the acetic acid concentration increases. PAN, the polymer with functional groups (-CN) which can form H-bonds, shows a higher affinity to water than to acetic acid. The sorption value measured for PSF in 100 % acetic acid might be a little too high. Due to the high degree of sorption of acetic acid the PSF samples become sticky and are therefore difficult to dry between tissue paper.

Table 10 *Total sorption (wt.%) obtained after 7 days of several polymers in acetic acid/water mixtures at 80 °C*

Polymer	0	20	50	80	100
		(wt.% Acetic acid)			
PSF	0.7	2.1	4.1	7.7	32.9
PEEK	0.6	1.7	3.2	6.7	9.9
PES	0.6	4.1	6.0	12.3	18.8
PAN	12.4	-	7.7	6.4	6.9
PVC	0.8	-	2.8	3.6	10.6

Sorption Selectivity

Besides the total mass uptake also the composition of the absorbed liquid in the polymer was determined as a function of the feed composition. The water content and the acetic acid content were determined independently. The acetic acid composition as a function of the feed composition is given in figures 6-8 for the polymers PAN, PVC and PSF, respectively.

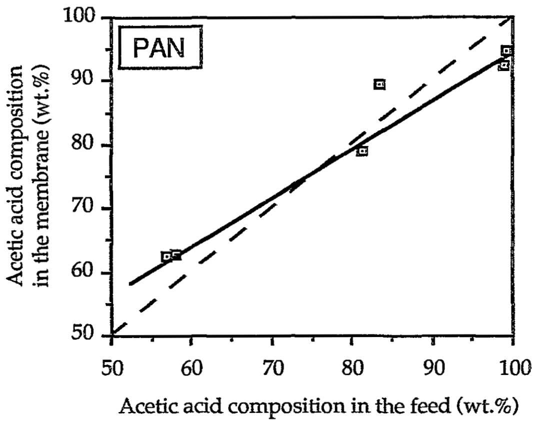


Figure 6 *Acetic acid composition in a PAN membrane as a function of the acetic acid composition in the feed mixture at 80 °C*

From figure 6 it can be concluded that the sorption selectivity of PAN is rather low and that dependent on the feed composition either a marginal preferential water sorption (above 75 wt.% acetic acid in the feed) or a marginal preferential acetic acid sorption (below 75 wt.% acetic acid in the feed) could be observed.

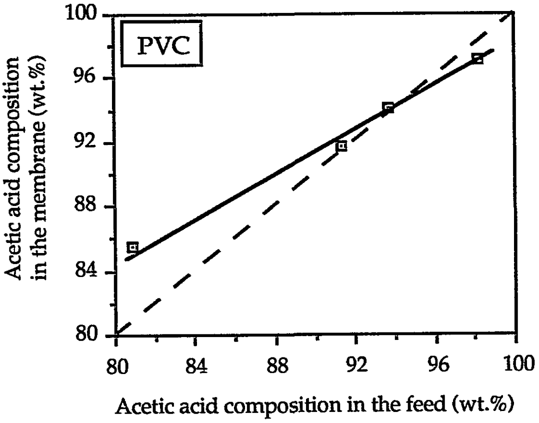


Figure 7 *Acetic acid composition in a PVC membrane as a function of the acetic acid composition in the feed mixture at 80 °C*

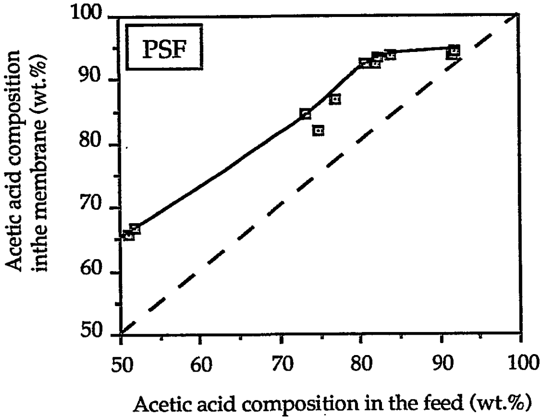


Figure 8 *Acetic acid composition in a PSF membrane as a function of the acetic acid composition in the feed mixture at 80 °C*

PVC (see figure 7) shows a similar behaviour as PAN (see figure 6); only the transition from preferential acetic acid sorption to preferential water sorption occurs at a much higher acetic acid concentration in the feed mixture (~ 95 wt.% acetic acid in the feed).

PSF (see figure 8) absorbs acetic acid preferentially over the entire feed composition studied. No reliable sorption data could be obtained in feed mixtures with a concentration higher than 92 wt.% acetic acid. The samples sticked together and broke into pieces due to the high degree of sorption.

From these experiments it can be concluded that PAN, PVC and PSF show a relatively low sorption selectivity, which means that pervaporation selectivity is completely determined by the difference in diffusion rate of water and acetic acid.

CONCLUSIONS

From the chemical stability experiments it can be concluded that PEEK, PSF and PES are the most resistant polymers in concentrated acetic acid at 80 °C. The weight average molecular weight of PVC immersed in concentrated acetic acid reduces in time, although the degree of dehydrochlorination of PVC is relatively low. On the other hand PAN seems to react with acetic acid.

From the pervaporation experiments using a feed of 80 wt.% acetic acid and 20 wt.% water at 80 °C it can be concluded that PVC, PAN, PAN-MA, PEEK, PI (Upilex S) and PSF are the most water selective polymers; they all have a permeate composition of less than 0.7 wt.% acetic acid. At higher concentrations of acetic acid in the feed mixture PAN appears to be the most selective polymer.

From sorption experiments it can be concluded that the mass uptake for PSF, PEEK, PES, and PVC increases with an increasing acetic acid content in the feed mixture. Only PAN, a polymer which contains a strong polar nitrile group and can form H-bonds with both water and acetic acid, shows a different behaviour; here the total sorption decreases upon increasing the acid concentration.

The sorption selectivity of PVC and PAN towards water is either larger or smaller than unity, dependent on the feed composition, which was varied from 50-100 % of acetic acid. In this range the sorption selectivity of PSF towards water was always somewhat smaller than unity, which means that PSF preferentially absorbs acetic acid. From these sorption selectivity experiments it can also be concluded that the pervaporation selectivity for water using these polymers is completely determined by the higher diffusion rate of water in comparison to acetic acid.

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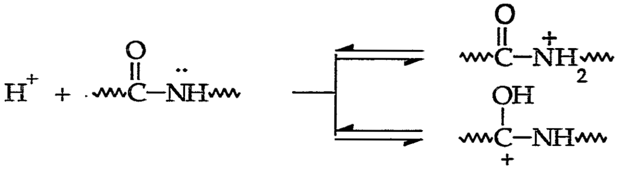
Appendix to Chapter 2

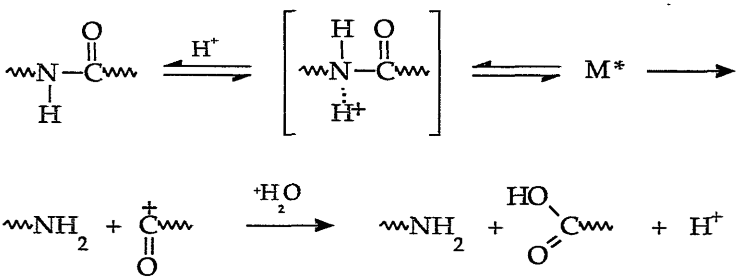
Chemical Resistance of Polymers in Acid Environments

polyamides(PA)

polyamides are not very stable in acid media. The electronic structure of the amido-bond indicates two possible ways in which protonation may occur, viz. at the amido nitrogen and at the carbonyl oxygen [A.1]:



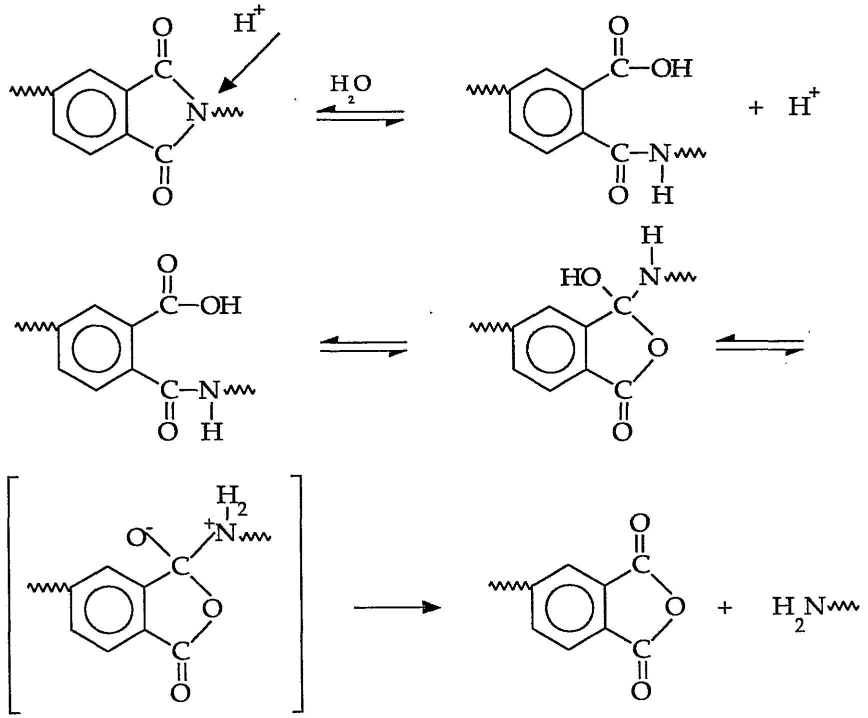
Protonation at the nitrogen atom prevails in less concentrated acids and results in further reaction, while protonation at the oxygen atom prevails in more concentrated acids, which form appears to be non-reactive. Because of the competition between protonation at the amido nitrogen and at the carbonyl oxygen, the hydrolytic *stability* of polymers with amido bonds increases with acid concentration. The decomposition of the majority of amides in acid media occurs by the mechanism [A.1]:



M* signifies an activated intermediate state

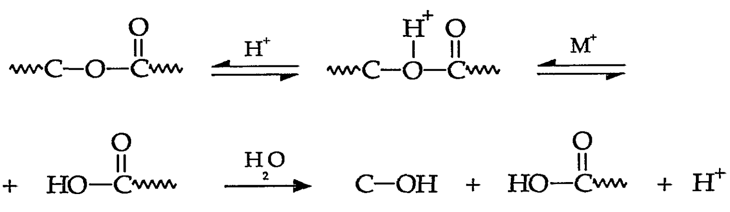
polyimide(PI)

Polyimides are chemically and thermally resistant polymers. Despite an excellent chemical resistance, PI can decompose in acid environments analogous to polyamides [A.2]:



polyesters

Polyesters also decompose in acid media. It is believed that decomposition occurs by protonation at the alkyl oxygen and follows the sequence [A.1, A.2]:

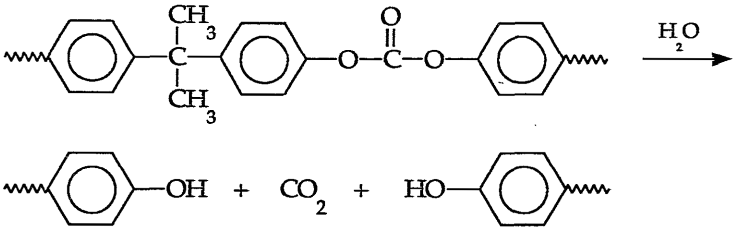


$$\sim\!C{-}O{-}\overset{\overset{O}{\|}}{C}\!\sim \underset{}{\overset{H^+}{\rightleftharpoons}} \sim\!C{-}\overset{\overset{H^+}{|}}{O}{-}\overset{\overset{O}{\|}}{C}\!\sim \overset{M^+}{\rightleftharpoons}$$

$$\sim\!C^+ + HO{-}\overset{\overset{O}{\|}}{C}\!\sim \xrightarrow{H_2O} C{-}OH + HO{-}\overset{\overset{O}{\|}}{C}\!\sim + H^+$$

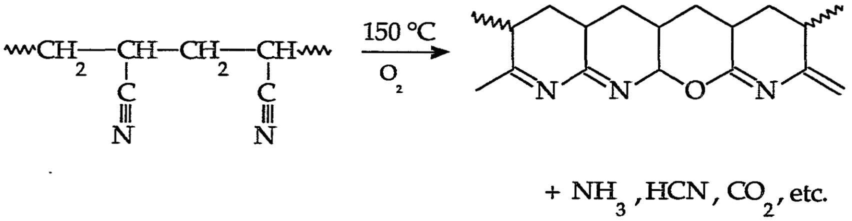
polycarbonate bisphenol-A (PC)

PC is rather resistant to hydrolysis. However at elevated temperatures and in the presence of trace amounts of water, i.e. ≥ 0.01 wt.%, PC can undergo rapid hydrolysis. Hydrolysis is accelerated strongly by bases and moderately by acids [A.2]:



polyacrylonitrile (PAN)

Although PAN is decomposed by concentrated alkalies and acids, PAN is resistant to dilute reagents and has a high UV resistance. PAN discolors upon heating above 150 °C, because of a cyclization reaction generating an insoluble ladder polymer. Cyclization is promoted by methacrylic acid and acryl amide, but impaired by styrene and vinyl acetate monomer units [A.2]. Cyclization can also be initiated by the presence of acids and phenols [A.3].



polyethers

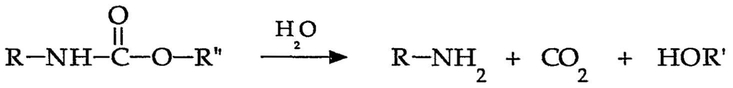
Generally, polyethers are very sensitive to acid-catalysed hydrolysis. Polyoxyalkylenes like, e.g. polyoxymethylene are more sensitive to acid-catalysed hydrolysis than polyoxy-3,5-dimethylphenylenes, which appear to be quite resistant, due to the protection of the ether bond by the methyl groups. Polyoxymethylene decomposes following the sequence [A.2].

$$\sim\!O-CH_2-O\!\sim \xrightarrow{H^+} \sim\!O-CH_2^{\;+} + HO\!\sim \xrightarrow{H_2O}$$

$$\sim\!O-CH_2OH + H^+$$

polyurethanes (PUR)

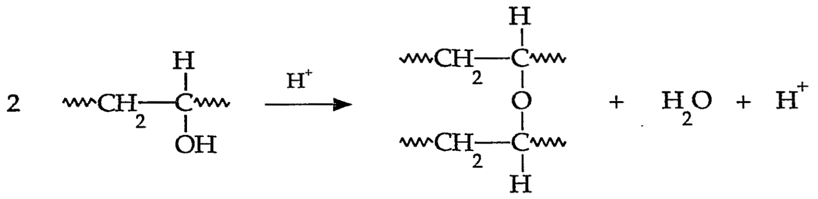
Even without the presence of acids, urethane-bonds decompose in aqueous solutions.



$$R{-}NH{-}\overset{\overset{\displaystyle O}{\parallel}}{C}{-}O{-}R'' \xrightarrow{H_2O} R{-}NH_2 + CO_2 + HOR'$$

polyvinylalcohol (PVA)

PVA can undergo crosslinking in acid media, which makes the polymer brittle [A.2]:



polyethylene(PE) and *polypropylene*(PP)

Polyolefins are slowly attacked by concentrated strong acids, such as sulfuric acid, nitric acid and chromic acid, especially if an oxidizing agent is present. Sulfuric acid sulfonates the amorphous domains of PP and more slowly of PE. At 100-125 °C concentrated sulfuric acid attacks PP and PE giving SO_2 as a by-product [A.2]. The stability in concentrated acetic acid is quite satisfactory.

polyvinylchloride(PVC)

Unplasticized PVC, the second largest volume thermoplastic, has a very high chemical resistance. PVC resists alkali, salt solutions, mineral acids and oxidizing acids, but is attacked by organic acids, especially acetic acid [A.4]. At moderate temperatures dehydrochlorination of PVC can take place which results in the formation of polyenes, crosslinking and possibly chain cleavage [A.5, A.6].

polymethylmethacrylate(PMMA)

PMMA has excellent weathering resistance and is only attacked by concentrated acids or alkalies [A.7].

polytetrafluoroethylene(PTFE)

PTFE, the largest volume fluoroplastic, is not melt processible and insoluble in all known liquid solvents. PTFE is resistant towards fuming sulfuric acid, nitric acid, aqueous reagents, strong bases and hydrogen peroxides [A.4].

Polyvinylfluoride(PVF)

PVF resists strong acids and bases and most common solvents, including hydrocarbons and chlorinated solvents, at room temperature. It is partially soluble in a few highly polar solvents at temperatures above 150 °C [A.4].

Polyvinylidenefluoride(PVDF)

PVDF resists most acids, but not fuming sulfuric or chlorosulfonic acid. Its resistance to inorganic bases is excellent till 120 °C and PVDF is resistant towards most organic bases except for some primary amines. The solvent resistance is excellent except to acetone and some other highly polar solvents. Furthermore, PVDF is resistant to halogens, oxidizing acids and inorganic salts [A.4].

polyoxy-3,5-dimethylphenylene(PPO)

PPO is a quite resistant polyether which decomposes thermally in an oxygen environment above 100 °C [A.2].

polysulfone(PSF)

PSF contains the same kind of ether bonds as PPO. Although, ether bonds are not very stable in strong acids, PSF appears to be well resistant towards glacial acetic acid [A.3], 50 % sulfuric acid and mineral acids. Furthermore, PSF is resistant towards alkali, and salt solutions and aliphatic hydrocarbons.

polyethersulfone(PES)

PES is even more resistant towards acids and other chemicals than PSF [A.3].

polyphenylenesulfide(PPS)

PPS has good chemical resistance except to strong oxidizing agents, sodium hypochlorite and mineral acids. PPS is insoluble in all known liquid solvents [A.4, A.8].

Poly-p-xylene

Poly-p-xylene polymers are resistant towards solvents, acids and bases. Besides their satisfactory chemical resistance poly-p-xylene polymers are also highly thermally resistant. Poly-p-xylene only dissolves in high boiling solvents such as α-chloro naphthalene above 200 °C [A.9], benzyl benzoate at 323 °C and p-terphenyl at 387 °C [A.10].

polyether-ether-ketone(PEEK)

PEEK is an extremely resistant polymer and as a result it is only soluble at room temperature in concentrated sulfuric acid, chlorosulfonic acid and methylsulfonic acid [A.11]. PEEK becomes sulfonated in concentrated sulfuric acid and chlorosulfonic acid. Sulfonation of PEEK makes the polymer soluble in other solvents like N,N-dimethylformamide (DMF) and dimethylsulfoxide (DMSO).

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3

INTEGRALLY SKINNED POLYSULFONE HOLLOW FIBER MEMBRANES FOR PERVAPORATION

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 favourable 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 [1] as well as the membrane morphology [2].

Kuraray Co, LTD [3] has patented a spinning process to prepare porous PSF hollow fiber membranes which can be used for water purification and blood filtration. In the spinning dope polyethylene glycol was used as an additive.

Henis and Tripodi [4,5] described a method how to prepare highly permselective and effectively high flux gas separation membranes from porous PSF hollow fiber membranes using a post-coating 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. [6-13] published extensively about the spinning process and the structure of PSF hollow fiber membranes for gas separation and applied the same coating procedure as Henis and Tripodi did [4,5] to obtain the required gas separation properties. By using Lewis at the interface has become so large that the vitrification boundary is crossed (figure 1, path 1) and a thin, dense toplayer is formed after solidification. During the interval of immersion and onset of phase separation not only the polymer concentration of the toplayer increases, but also to a smaller extent the polymer concentration in the sublayer. This goes on till the toplayer 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 toplayer (figure 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.

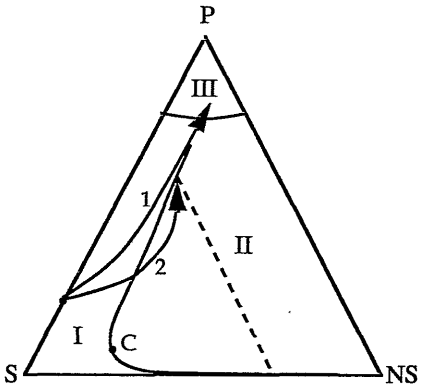


Figure 1. *Schematic representation of the precipitation process. I. homogeneous polymer solution; II. liquid-liquid demixing region; III.gel or vitrification area; C is critical point; 1 possible composition path of the toplayer; 2 possible composition path of the sublayer.*

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), N,N-

Dimethylformamide (DMF) or Formylpyperidine (FP) as solvent and glycerol, iso-propanol, butanol or pentanol as nonsolvent.

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 toplayers 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 toplayer 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 [21, 22] 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 airgap and by a bore coagulant at the inside.

An ideal membrane for pervaporation is a membrane with a very thin defect-free toplayer 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 [18, 19].

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 toplayer 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 toplayer and short enough to obtain a toplayer 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 toplayer is fixed.

In order to achieve a porous low resistant sublayer additives (e.g. nonsolvents) can be added to the spinning dope, i) to make the polymer solution more sensitive to nonsolvent inflow or ii) 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

Pre-dried polysulfone 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 research group at Twente University with a tube and two orifices [20] (figure 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 hours. Subsequently, the fibers were immersed in an ethanol bath for at least 5 hours followed by immersion in a hexane bath for another 5 hours. At last the fibers were dried in air at room temperature. The spinning speed varied from 3.5 to 5 m/min.

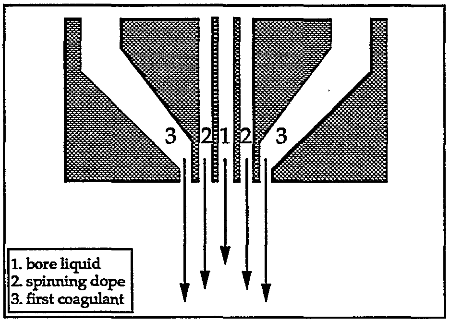


Figure 2 *Schematic representation of the triple orifice spinneret*

Delayed Demixing

Delay times of demixing could be measured by a simple light transmission technique as described by Reuvers et al. [21] and van 't Hof et al. [18]. 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 for nonsolvents which 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 hours. Steady state was normally obtained after 2-3 hours. the permeate was analysed using a Varian 3700 Gas Chromatograph filled with a Poropack Q column at a temperature of 190 °C. A schematic representation of the pervaporation set-up is given in figure 3.

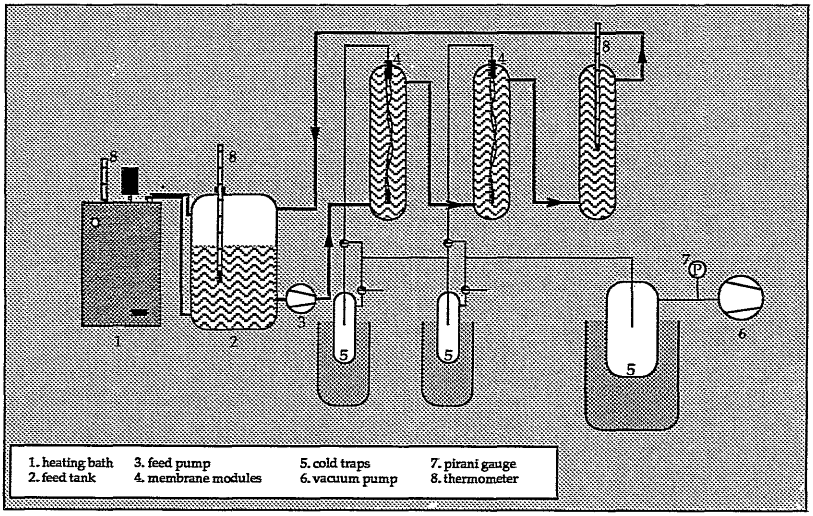


Figure 3 *Schematic representation of the pervaporation set-up*

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 toplayer 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 will be, and the denser and thicker the interfacial layer will become. A defect-free layer is required to obtain the intrinsic selectivity of the polymer material.

Table 1. *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.%.

Table 1 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 [23].

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 1 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 2 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 2 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 1). The lower selectivities are accompanied by higher fluxes, which is a normal behaviour.

Table 2. *Selectivity and flux of PSF hollow fiber membranes for the dehydration of 80 wt.% acetic acid in water at 70 °C; 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*

First nonsolvent bath	Contact time 1^e bath (s)	Selectivity	Flux (kg/m^2h)
Pentanol	5.7	53	0.084
Glycerol	0.82	42	0.130
80% Glycerol/ 20% I-PrOH**	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

* intrinsic selectivity of PSF is $\alpha = 620$

** I-PrOH = iso-propanol

% = vol.%.

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 toplayer. 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 toplayer.

Considering the ease of spinning, a nonsolvent with a lower viscosity as a first coagulant shows a more continuous and better controllable flow. Since the mixture 80/20 wt.% glycerol/iso-propanol results in higher selectivities compared to mixtures which 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 chapter have been spun using this mixture as a first coagulant.

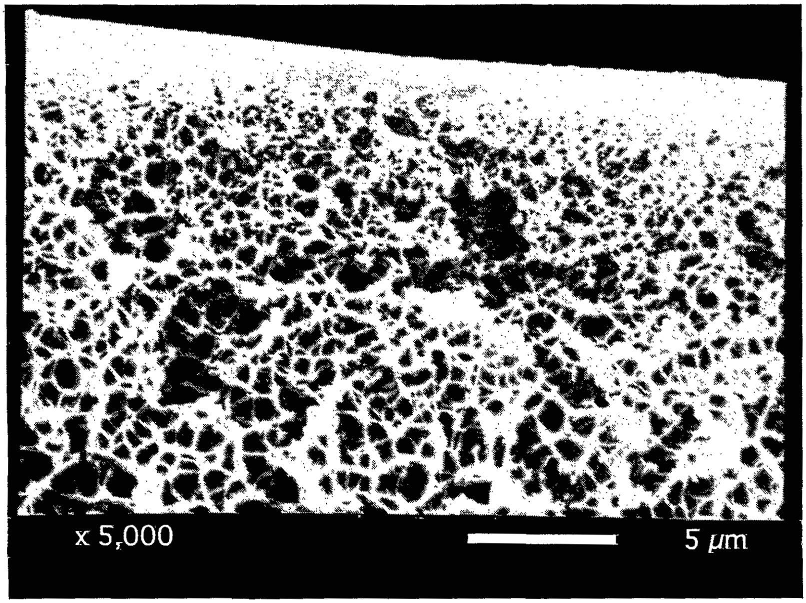


Figure 4 *Cross section and toplayer of a PSF hollow fiber membrane, Spinning dope: 35 wt.% PSF; 62 wt.% NMP; 3 wt.% glycerol*

SEM pictures (see figure 4) of the hollow fiber membranes spun from a solution containing 35 wt.% PSF, 3 wt.% glycerol and 62 wt.% NMP showed a rather closed cell structure and a relatively dense layer at the bore side (figure 9a). 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 2. According to the SEM picture the toplayer is about 1.4 μm thick, which means that if the substructure had no transport resistance at all the flux should be about 0.46 kg/m^{2}h instead of 0.13 kg/m^{2}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 °C; an intrinsic selectivity of α = 620 and an intrinsic permeability of P = 0.65 x10^{-6} 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 (χ_{23}), nonsolvent and polymer (χ_{13}) and nonsolvent and solvent (χ_{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.

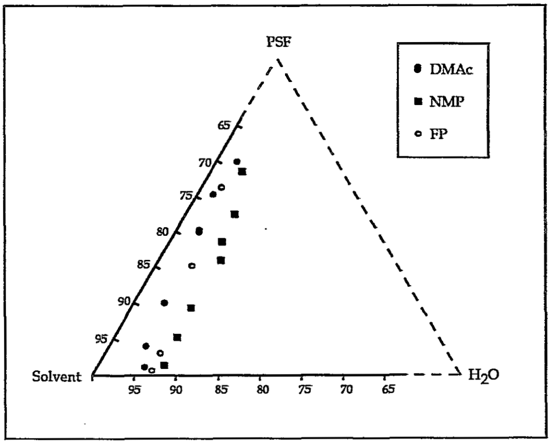


Figure 5 *Ternary phase diagram for the systems: PSF/NMP/H_2O [24] PSF/DMAc/H_2O [24] and PSF/FP/H_2O.*

The data for DMAc and NMP are obtained from literature [24] and the data for FP are determined by cloud point measurements using a simple titration technique as used by others. [25-27].

When the interaction between solvent and nonsolvent decreases (DMAc > FP > 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, χ_{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 3

Table 3. *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^3/mol)
Formylpiperidine	201,750	111.05
N-methylpyrrolidone	44,000	95.96
Dimethylacetamide	17,300	92.98

* data from Kesting et al. [11]

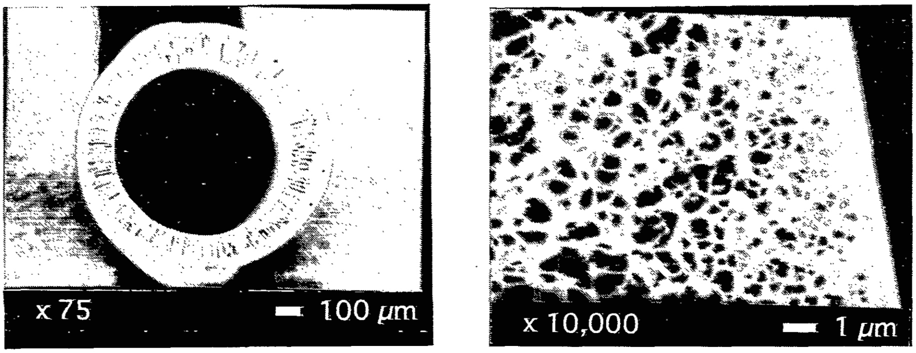
Fibers have been spun using a solution of 30 wt.% PSF in the three solvents given in table 3. The spinning temperature was 48 °C, as first nonsolvent a mixture of 80 vol.% glycerol and 20 vol.% iso-propanol was used, whereas water was used as second nonsolvent and as bore liquid.

The pervaporation results represented in table 4 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 figure. 6) and DMAc (see figure. 7), which might explain their similar separation behaviour.

Table 4. *Selectivity and flux of PSF hollow fiber membranes for the dehydration of 80 wt.% acetic acid in water at 70 °C; fibers are spun using various solvents in the spinning dope and no additive*

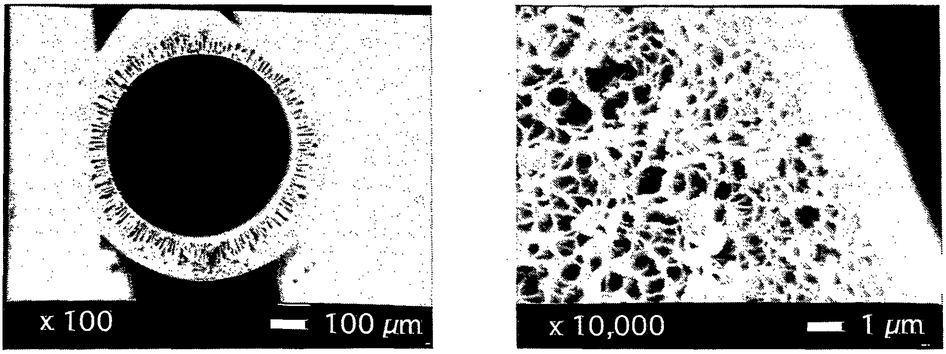
PSF (wt.%)	Solvent	Spinning temp. (°C)	Contact time 1^e bath (s)	Selectivity	Flux (kg/m^2h)
30	NMP	48	0.80	54.1	0.222
30	DMAc	48	0.68	59.8	0.193
30	FP	48	1.28	5.2	0.326

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



cross section
outside toplayer

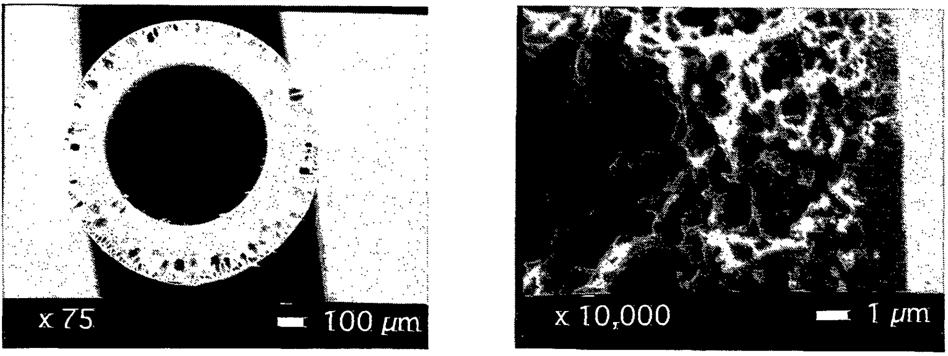
Figure 6 *Cross section and toplayer of a PSF hollow fiber membrane; Spinning dope: 30 wt.% PSF; 70 wt.% NMP, bore liquid: water first nonsolvent: 80/20 vol.% glycerol/i-propanol; second nonsolvent: water*



cross section

outside toplayer

Figure 7 *Cross section and toplayer 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*



cross section

outside toplayer

Figure 8 *Cross section and toplayer 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*

The structures shown in figures 6 and 7 are typical structures obtained in a dual bath spinning process [18, 19]: 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 favourable for macrovoid formation, following the pattern as explained earlier (theoretical section,[21, 22]). The macrovoids do not extent 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 toplayer delayed demixing takes place. Since there is a relatively large outflow of solvent compared to the inflow of nonsolvent the polymer concentration at the interphase increases and a dense toplayer results.

A completely different structure can be observed when FP is used as a solvent (see figure 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), since the binodal with FP as solvent lies in between the binodals when NMP or DMAc are used (see figure 5). The only difference between DMAc, NMP and FP is the larger molar volume of the solvent and the high viscosity of the 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 favoured 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 change. Since the polymer solution has not increased much in concentration, conditions are quite favourable 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 ultra-thin toplayer 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 favours a more open structure of the sublayer.

Addition of a nonsolvent to the spinning dope can also suppress the formation of macrovoids [18,22]. 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.

Table 5. *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^e bath (s)	Selectivity	Flux (kg/m^{2}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

In table 5 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. Outdiffusion of a very small amount of solvent and/or indiffusion of a very small amount of nonsolvent at the toplayer (outside) of the fiber is enough to cross the binodal and result in liquid-liquid demixing, so that a defect-free toplayer 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 [22,28]. 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 6.

Table 6. *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 1e bath (s)	Selectivity	Flux (kg/m^{2}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

The temperature of the spinning dope during the spinning process was varied with the initial polymer concentration because a certain minimum viscosity is necessary for a constant extrusion rate of the spinning dope.

Table 6 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.

Effect of Bore Liquid Composition

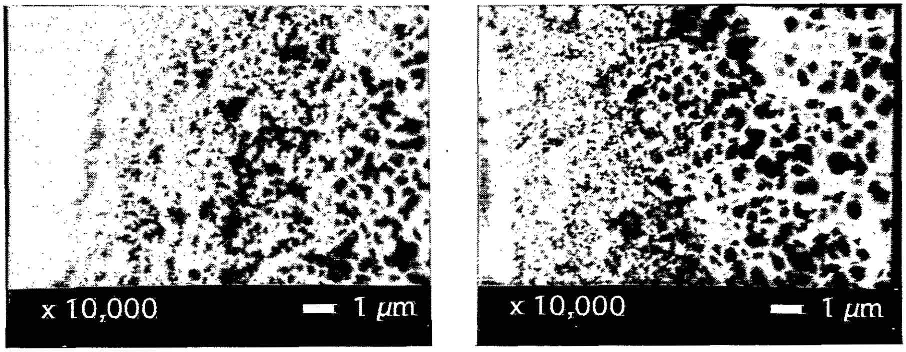
From SEM pictures it can be clearly seen that the layer formed at the inside of the hollow fiber is quite dense compared to the rest of the structure (see figure 9a). The higher the polymer concentration in the spinning dope the denser this layer and consequently the higher the resistance will be. In 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 7.

Table 7. *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_2O)*

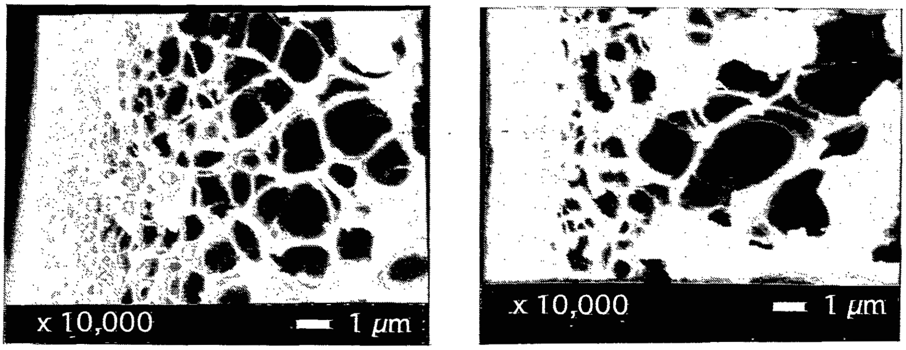
Spinning dope			Bore liquid				
PSF (wt.%)	Glycerol (wt.%)	NMP (wt.%)	H_2O (wt.%)	NMP (wt.%)	Contact time 1^e bath (s)	Selectivity	Flux (kg/m^{2}h)
35	3	62	100	0	1.12	44.1	0.132
35	3	62	40	60	1.08	45.9	0.141
35	3	62	35	65	1.03	44.0	0.240
35	3	62	30	70	1.18	54.0	0.374

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

Table 7 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.



9a). Bore liquid: 100% H_2O 9b). Bore liquid: 30% H_2O/70% NMP

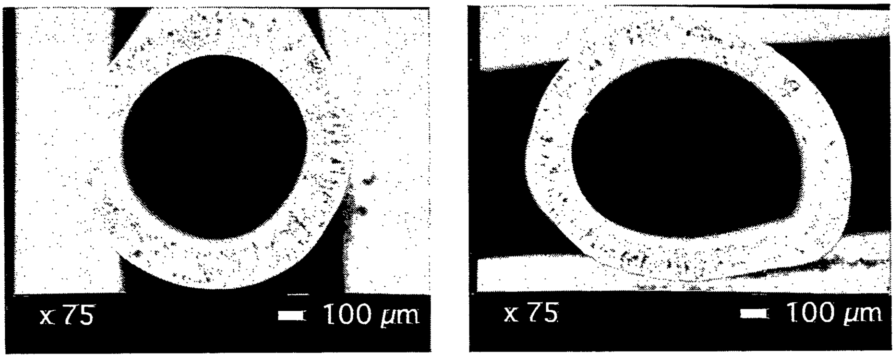


9c). Bore liquid: 25% H_2O/75% NMP 9d). Bore liquid: 20% H_2O/80% NMP

Figure 9 *Toplayer structure at the bore side of the PSF hollow fiber membrane as a function of the ratio NMP/H_2O 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

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 can not be controlled anymore and the fibers loose 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.



25 wt.% water/75 wt.% NMP

20 wt.% water/80 wt.% NMP

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*

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

Although the selectivities of the PSF hollow fiber membranes are acceptable (α = 65-80) they never reached the intrinsic value of α = 620, measured for homogeneous flat membranes of a thickness of 20 μm. The

From table 1 it can be concluded that when a flux of 0.5 kg/m^2h 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 in this chapter 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 pure water at the outside of the fiber. In figure 1 a schematic representation of both experiments is represented.

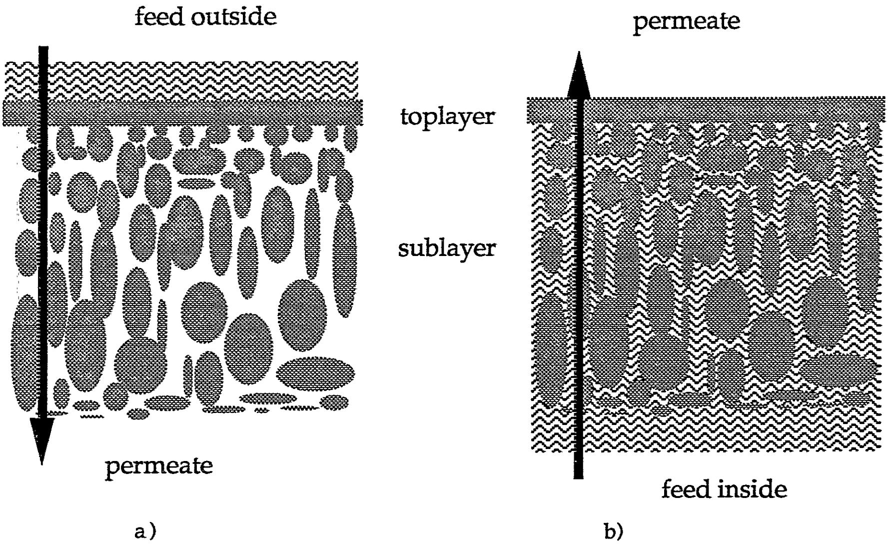


Figure 1 Schematic representation of a pervaporation experiment with pure water a.) feed at the outside; b.) feed at the inside

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

$$J_{H_2O} = \frac{1}{R_{H_2O}} (P_{feed} - P_{perm.}) \qquad (A6)$$

where: $P_{feed} = C_{H_2O} \cdot \gamma_{H_2O} \cdot P_{s,H_2O}$

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

$P_{s,H_2O} = 2.64 \times 10^3 \; N/m^2$

$C_{H_2O} = 1$

$\gamma_{H_2O} = 1$

It is assumed that the membrane surface area A at the outside is the same as at the inside. The results of the pervaporation experiment as well as of the calculated membrane resistances are represented in table 2.

Table 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^2h)	63	77
	62	78
Membrane resistance (m/s)	4.19×10^4	3.43×10^4
	4.26×10^4	3.38×10^4

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 figure 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 2 it can be calculated that the resistance of the sublayer is 19% ± 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

		unity
A	dimensionless friction parameter	
A	membrane surface area	m^2
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^2s
f	Fanning friction factor	
γ	activity coefficient	
K	optimum flux at permeate pressure zero	kg/m^2h
L	fiber length	m
m	permeate mass flow rate	kg/s
M	molecular weight	kg/mol
p	pressure	N/m^2
p_0	pressure at the dead end of a hollow fiber	N/m^2
p_L	pressure at the fiber mouth	N/m2
P_s	saturation pressure	N/m2
ρ	density	Kg/m^3
R	gas constant	J/mol K
R_{H_2O}	water transport resistance	m/s
T	temperature	K
μ	viscosity	kg/m s
v	velocity	m/s
z	distance	m

indices

feed	feed side	perm.	permeate side

Reference

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4

SELECTIVITY AS A FUNCTION OF MEMBRANE THICKNESS
Gas separation and pervaporation

INTRODUCTION

Transport of gases, vapours and liquids through homogeneous films can be described by a "solution-diffusion mechanism" as developed by Lonsdale et al. [1]. According to this model transport takes place by sorption of the components into the membrane material at the feed side, followed by diffusion through the membrane, due to a chemical potential difference across the membrane, and desorption at the permeate side. Fick's law has been used as a basis for this model, which describes the component flux through the membrane as being proportional to the reciprocal membrane thickness. Because this relation is valid for both components of a binary mixture selectivity should be independent of the membrane thickness. This should be the case for liquid and gas mixtures.

In the case of pervaporation the influence of membrane thickness on selectivity and flux was only studied by a few people. Binning [2] was one of the first and he concluded that the flux of a mixture of n-heptane and iso-octane (50/50 vol.%) through a plastic film was proportional to the reciprocal membrane thickness and the selectivity was indeed independent of the thickness for membrane thicknesses in the range of 20-50 µm.

Brun et al. [3] studied the influence of membrane thickness on selectivity using nitrile rubber membranes and a 60/40 mixture of butadiene and iso-butene. They concluded that the selectivity was constant above a membrane thickness of 100 µm; a lower selectivity for membrane thicknesses of around 17 µm was observed, especially at relatively high downstream pressures. This phenomenon was explained by assuming that elastomers are composed of very thin grains (0.5-5 µm), which results in the formation of micropores in the membrane. Diffusion through these micropores becomes important in the case of thin membranes resulting in a reduction of selectivity; the effect of these pores can be neglected in the case of thick membranes. Compaction of the membrane material due to a high pressure applied on the film results in the disappearance of micropores. Nevertheless, an influence of membrane thickness on selectivity could still be observed.

Spitzen [4] studied the separation of water/ethanol mixtures as a function of the membrane thickness using polyacrylonitrile (PAN) as membrane material. He observed that at thicknesses below 20 μm the selectivity dropped drastically. Reduction of the evaporation rate of the solvent from the casted film resulted in somewhat higher selectivities for thin membranes, but still a drop in selectivity could be observed with decreasing membrane thickness. Spitzen attributes this mainly to artefacts in the membranes.

In chapter 3 of this thesis the preparation of asymmetric integrally skinned PSF hollow fiber membranes has been described. The selectivity of these membranes, with toplayer thicknesses of 0.8-1.5 μm, for the dehydration of 80/20 wt.% acetic acid/water solution at 80 °C varied between $\alpha = 60\text{-}80$, while a selectivity of $\alpha = 620$ has been measured as the intrinsic selectivity of PSF (chapter 2).

Aptel et al. [5] observed a reduction of selectivity as a function of decreasing membrane thickness for grafted polytetrafluoroethylene films using a water/dioxane mixture and Mulder [6] observed the same behaviour for cellulose acetate membranes using a 50/50 wt.% mixture of ethanol and water.

It can be concluded that the transport of liquid mixtures does not (always) obey Fick's law since the selectivity is a function of the membrane thickness. It seems that a minimum thickness is required to obtain intrinsic selectivity and below this thickness selectivity starts to decrease with decreasing thickness.

On the other hand for gas separation some investigators have shown [7,8] that the intrinsic selectivity can be maintained even for thicknesses less than 500 nm. This was found for quite a number of different materials such as polysulfone, polyimide, polyetherimide, modified polyphenyleneoxyde and polycarbonate. Although transport in both pervaporation and gas separation takes place according to the solution-diffusion model there seem to be inherently differences, due to differences in affinity of gases and liquids towards polymers.

In this chapter the pervaporation selectivity is studied as a function of the membrane thickness for three different materials, viz. polysulfone (PSF), polyvinylchloride (PVC) and polyacrylonitrile (PAN), and the decline in selectivity below a certain minimum thickness will be discussed. Except for pervaporation, PSF and PVC have also been tested for gas separation as a function of membrane thickness and a comparison between gas separation and pervaporation has been made with respect to selectivity.

EXPERIMENTAL

Materials

Polyacrylonitrile (PAN-7A) was obtained from Du Pont, polysulfone (PSF, Udel P3500) from Amoco and polyvinylchloride (PVC, high Mw) from Aldrich. The solvents N,N-dimethylformamide and tetrahydrofuran were of analytical grade and were obtained from Merck.

Membrane Preparation

Membranes were prepared by solution casting on a glass plate followed by evaporation of the solvent in a nitrogen atmosphere. After the solvent had evaporated the membranes were further dried in a vacuum oven at 80 °C (PVC and PAN) and at 150 °C (PSF) for 1 week, before they were measured for pervaporation. Only the PSF membranes were applied to a heat treatment above the glass transition temperature (1 hour at 210 °C) to improve their stability against environmental or solvent induced stress-cracking.

Gas Separation

Gas separation experiments were carried out using a 75/25 vol% CH_4/CO_2 mixture at room temperature and a pressure difference across the membranes of 6 bars. The set-up used is totally automized and the permeability was calculated by an accurate measurement of the pressure increase with time in a calibrated volume at the downstream side of the membrane. The selectivity was determined by gas chromatographic analysis of the permeate samples.

Pervaporation

Pervaporation experiments were carried out using the same set-up as described in chapter 2. The permeate side was maintained at a pressure of 0.1-0.5 mmHg by a Crompton Parkinson vacuum pump. The pressure was measured by an Edwards pirani meter. Permeate samples were taken every hour, during 8 hours. Steady state was normally obtained after 2 to 3 hours. The permeate was analysed using a Varian 3700 Gas Chromatograph filled with a Poropack Q column at a temperature of 190 °C.

RESULTS AND DISCUSSION

Gas Separation

Asymmetric integrally skinned PSF hollow fiber membranes as well as homogeneous PSF and PVC membranes with variable thicknesses have been measured for the separation of a CH_4/CO_2 gas mixture. The selectivity and P/l values of four different PSF hollow fiber membranes are given in table 1.

Table 1 *Selectivity and P/l values of different PSF hollow fiber membranes as a function of the effective thickness*

Membrane nr.	Selectivity	P/l* (CO_2)	Effective thickness (μm)
1	30.3	3.7	2.2
2	33.0	4.9	1.7
3	30.8	6.5	1.3
4	33.1	10.3	0.8

* P/l: 10^{-6} cm^3/cm^2. s. cmHg

The hollow fiber membranes represented in table 1 differ from each other with respect to the polymer concentration and additive concentration used in the spinning dope. The effective membrane thickness of the hollow fibers has been calculated from the P/l values and a permeability of 8.3 Barrer for PSF, which was obtained from measurements using homogeneous membranes with known thicknesses (table 2).

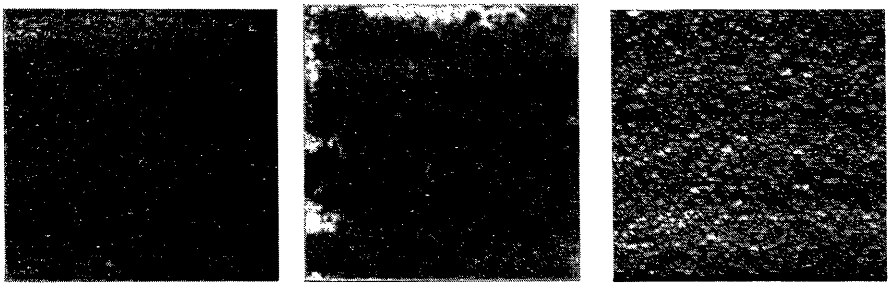
In table 2 the selectivity and permeability of homogeneous PSF and PVC membranes are represented as a function of the membrane thickness.

Table 2 *Selectivity and P/l values of homogeneous PSF and PVC membranes as a function of the membrane thickness*

Membrane	Thickness (μm)	Selectivity $\alpha(CO_2/CH_4)$	P/l* (CO_2)
PSF	34	32.5	0.245
PSF	2.7	30.0	3.11
PVC	20	31.8	0.014
PVC	13	32.7	0.023
PVC	4	12.2	0.139

* P/l: 10^{-6} cm^3/cm^2. s. cmHg

From the results in the tables 1 and 2 it can be concluded that for PSF the selectivity for the separation of CO_2/CH_4 gas mixtures is independent of the membrane thickness. In the case of PVC the intrinsic selectivity could not be obtained anymore below a certain thickness (± 4 μm).



PSF (surface area 3 x 3 μm) PVC (surface area 6 x 6 μm) PAN (surface area 6 x 6 μm)

Figure 1 *Atomic force microscope pictures of the top-surface of PSF, PVC and PAN films with a thickness of 6-9 μm; PSF and PVC are casted from a tetrahydrofuran solution and PAN from a N,N-dimethylformamide solution*

This can be explained by the relatively large defects in the PVC film introduced during evaporation of the solvent, which can be seen from the atomic force microscope pictures represented in figure 1. Defects with a depth of more than 0.5 μm could be observed. Due to the low permeability of PVC a small single defect already has a large effect on the selectivity. The surface defects of PSF are much smaller and therefore do not affect the selectivity in gas separation, while PAN does not show surface defects at all; due to the fact that PAN is a semi-crystalline polymer an aggregate surface structure has been formed.

The P/l values in table 2 show a linear relationship as a function of the reciprocal membrane thickness, except for the 4 μm thick PVC film. This is in perfect agreement with the solution-diffusion model: the gas flux is proportional to the reciprocal membrane thickness and selectivity is independent of the membrane thickness.

Pervaporation

As already described in the introduction, the pervaporation selectivity seems to become dependent on membrane thickness below a certain thickness. Asymmetric hollow fibers of PSF (chapter 3) with thin toplayers have been prepared and did by far not reach the intrinsic selectivity whereas in the case of gas separation no reduction in selectivity was observed.

In order to neglect the influence of the porous support homogeneous flat membranes have been prepared of PSF, PVC and PAN. The selectivity and flux as a function of membrane thickness was studied for the dehydration of 80 wt.% acetic acid at 80 °C. The permeate composition as a function of membrane thickness is given in figure 2. This figure shows that for PSF, PVC as well as for PAN the water concentration in the permeate is constant above a certain minimum thickness. Below this thickness the water content decreases as the membrane thickness decreases, which results in a drop of the selectivity. It can also be concluded that the effect is large in the case of PSF and PAN and much smaller in the case of PVC.

In the figures 3 to 5 the total flux as well as the component fluxes are plotted as a function of the reciprocal membrane thickness for PSF, PVC and PAN, respectively. Many membranes have been prepared and measured, especially for thicknesses below 10 μm. Membranes containing pin holes could be easily recognized; the total flux of these membranes was too high and did not fit to the curve of total flux versus reciprocal

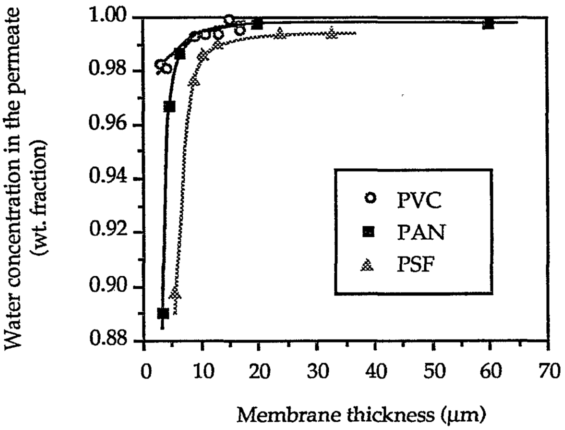


Figure 2 *Water content in the permeate as a function of membrane thickness for the dehydration of 80/20 wt.% acetic acid/water at 80 °C by pervaporation*

membrane thickness; besides the selectivity was extremely low in these cases.

The figures 3a to 5a show a nice linear relationship between the total flux and the reciprocal membrane thickness as is predicted by the solution-diffusion model (Fickian behaviour). Splitting up the total flux in the component fluxes of water and acetic acid it can be clearly seen how the selectivity decreases with decreasing membrane thickness. The water flux shows a similar Fickian behaviour as the total flux, while the acetic acid flux shows a non-Fickian behaviour; the acetic acid flux increases more than proportionally with decreasing membrane thickness in the case of PVC and even exponentially in the cases of PSF and PAN.

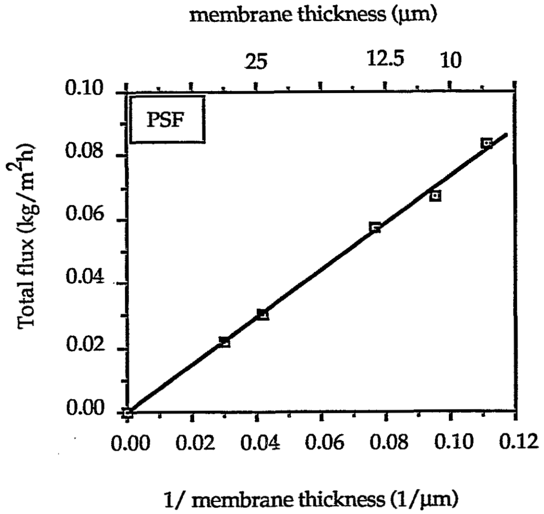


figure 3a.

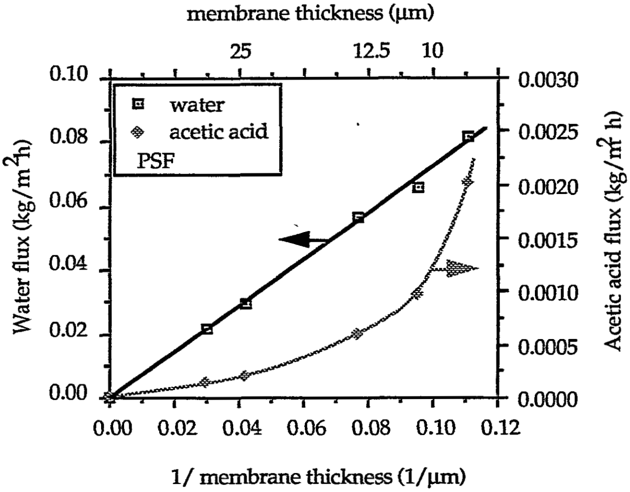


figure 3b.

Figure 3 *Total flux (a) and component fluxes (b) as a function of the reciprocal PSF membrane thickness for the dehydration of a 80/20 wt.% acetic acid/water mixture at 80 °C; note the different scales on the vertical axis.*

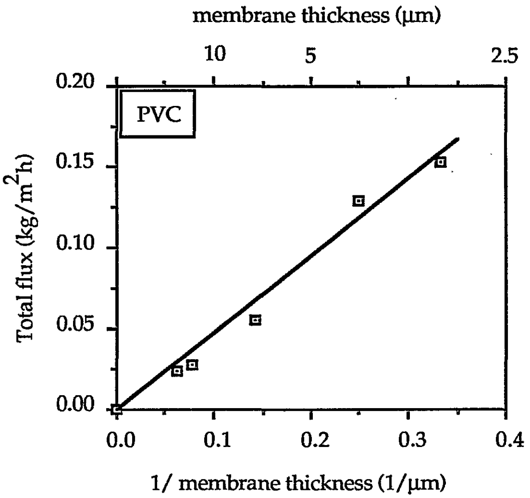


figure 4a.

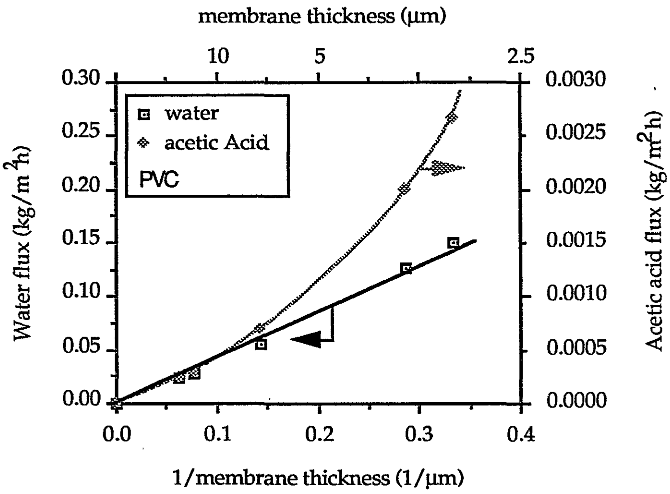


figure 4b.

Figure 4 *Total flux (a) and component fluxes (b) as a function of the reciprocal PVC membrane thickness for the dehydration of a 80/20 wt.% acetic acid/water mixture at 80 °C*

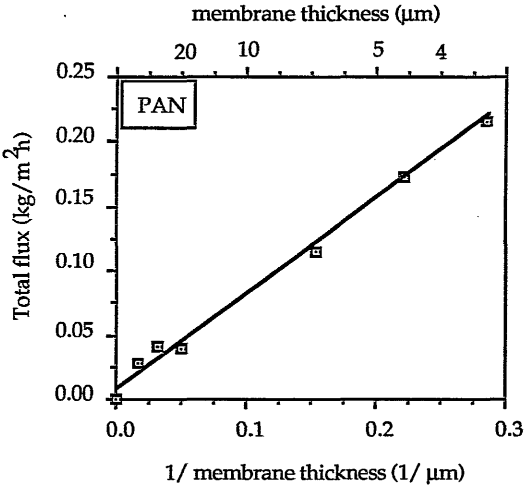


figure 5a.

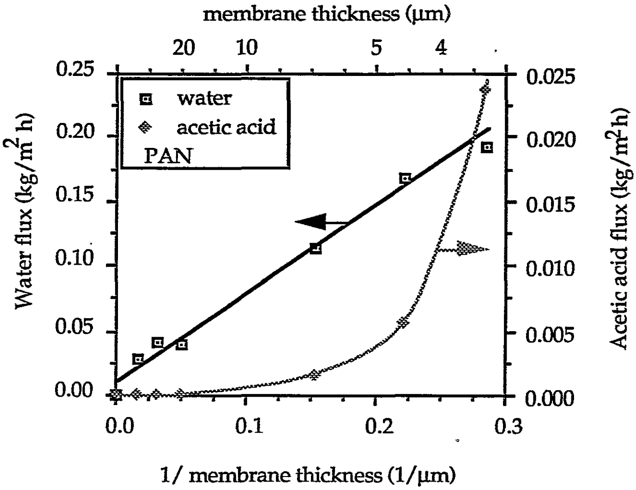


figure 5b.

Figure 5 *Total flux (a) and component fluxes (b) as a function of the reciprocal PAN membrane thickness for the dehydration of a 80/20 wt.% acetic acid/water mixture at 80 °C*

Due to the high water selectivity of the membrane material the acetic acid flux is two orders of magnitude smaller compared to the water flux for a 20 μm thick membrane. Therefore, the total flux is completely controlled by the water flux. Even an exponential increase of the acetic acid flux hardly influences the total flux, but does influence the selectivity.

Pervaporation experiments have also been carried out using pure components as the feed. In figure 6 the pure water flux and the pure acetic acid flux are given as a function of the reciprocal thickness of a PVC membrane.

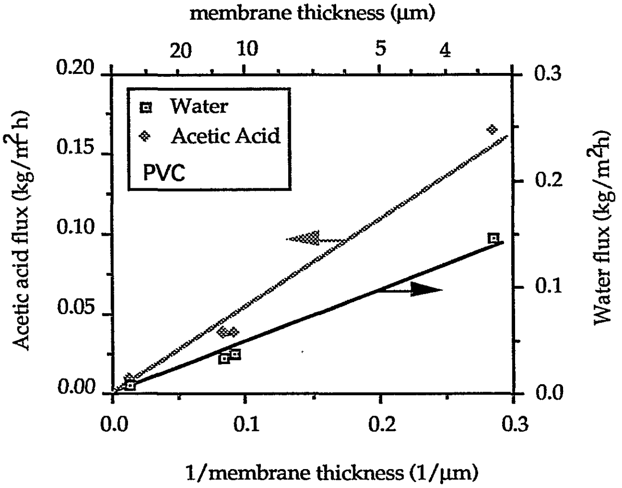


Figure 6 *Pure water flux and pure acetic acid flux as a function of the reciprocal membrane thickness for PVC*

Figure 6 shows a Fickian behaviour for both components. It can be seen that the pure acetic acid flux is much higher than when a mixture of 80/20 wt.% acetic acid/water (see figure 4b) is used as the feed. The addition of water to acetic acid reduces the acetic acid flux by more than 2 orders of magnitude. This is caused by the lower sorption behaviour, but also the cluster formation of acetic acid in the presence of water may contribute to a lower diffusivity.

Membrane Morphology

In thin film preparation the evaporation of the solvent will proceed faster than in the case of thick films. This difference in evaporation rate might result in a different morphology of the ultimate membrane; a higher rate of evaporation gives the polymer chains less time to achieve the optimal packing. A heat treatment above the glass transition temperature should result in the optimal packing density after all, due to a rearrangement of the polymer chains (relaxation), and morphology differences will probably disappear. Of the studied polymer membranes only the PSF membranes were applied to a heat treatment above their glass transition temperature (1 hour at 210 °C) in order to improve the resistance against environmental stress-cracking.

To see whether thin films have a different morphology which might explain a lower selectivity several thin films were stacked together, measured for pervaporation and compared to a single membrane of similar total thickness. In table 3 the selectivity and flux are given of single-layer and multi-layer membranes of PSF and PVC for the dehydration of 80 wt.% acetic acid at 80 °C.

Table 3 *Selectivity and flux of PSF and PVC single- and multi-layer membranes of different thicknesses for the dehydration of 80 wt.% acetic acid at 80 °C*

Polymer	Layer thickness (µm)	Number of layers	Total thickness (µm)	Feed (wt.% acid)	Permeate (wt.% acid)	α	Flux (kg/m^{2}h)
PSF	33	1	33	80.30	0.60	675	0.022
PSF	9	4	36	79.60	1.50	256	0.022
PSF	9	1	9	80.10	2.40	164	0.084
PVC	11	1	11	79.50	0.80	481	0.034
PVC	3	4	12	79.70	1.00	389	0.034
PVC	3	1	3	80.40	1.70	237	0.152

From table 3 it can be seen that in the case of PVC the selectivity of the multi-layer membranes are similar to that of a (single-layer) membrane with an equal total thickness. However, the selectivity of one membrane with the same thickness as one layer of the multi-layer membrane is lower.

The permeate composition of the PSF multi-layer membrane is in between the value of the thin and the thick single-layer membrane. If the morphology determines the low selectivity of thin membranes the selectivity of the multi-layer membrane should have the same value as the thin membrane. Therefore, a lower selectivity for thin membranes cannot be explained by a difference in polymer morphology. Besides, morphology differences should not be present anymore in the PSF membranes due to the heat treatment above the glass transition temperature; nevertheless the selectivity of these membranes appeared to be dependent on thickness as well (see figure 2).

These multi-layer experiments together with the pervaporation experiments, where the selectivity of homogeneous PSF, PVC and PAN was studied as a function of membrane thickness confirm the hypothesis that selectivity becomes dependent on the membrane thickness below a certain limiting thickness and is not determined by morphology differences. This limiting thickness has a value of around 20 μm. Above this thickness selectivity is independent of the membrane thickness which is in accordance with the solution-diffusion theory.

The defects observed in PVC films by atomic force microscopy which result in a lowering of the selectivity for gas separation when thin films are used might also be responsible for the decrease in selectivity observed for pervaporation using thin films. With PSF membranes the selectivity is found to be independent on membrane thickness for gas separation, while in the case of pervaporation a thickness dependency has been observed. An explanation for this phenomenon has to be found in differences in sorption and diffusion between pervaporation and gas separation. The influence of desorption is neglected.

Comparing pervaporation and gas separation three major differences can be distinguished, viz. relatively strong *mutual interactions* between the various components, *coupling* of the permeating components, and a higher *affinity* (thermodynamic interaction) between penetrants and polymer, all occurring in the case of pervaporation.

Thermodynamic Interaction and Coupling

Phenomena which can be neglected in gas separation but might play an important role in pervaporation are thermodynamic interaction and coupling. Thermodynamic interaction represents the interaction of the permeating components with the membrane material and coupling represents the influence of the flow of one component on the flow of the other components.

Thermodynamic interaction plays an important role in sorption selectivity. A higher affinity of the membrane material with component i compared to component j mostly results in preferential sorption of component i; besides interaction, free entropy of mixing plays a role as well. In table 4 the sorption selectivities of PSF, PAN and PVC for two different acetic acid/water mixtures are represented.

Table 4 *Sorption selectivity of PSF, PAN and PVC as a function of the acetic acid/water composition*

Polymer	Water in Feed (wt.%)	Sorption Selectivity ($\alpha^S_{H_2O}$)
PSF	10	0.58
PSF	20	0.44
PAN	10	1.47
PAN	20	1.06
PVC	10	0.86
PVC	20	0.71

Data from chapter 2

From table 4 it can be concluded that PSF and PVC absorb acetic acid preferentially, despite the fact that they are highly water selective in pervaporation. PAN absorbs water preferentially, but has only a low sorption selectivity. This means that pervaporation selectivity is completely determined by the difference in diffusion of water and acetic acid; water the smaller component has a higher diffusion rate than acetic acid.

The affinity between the components and the polymer is rather low as can be concluded from the relatively low degree of sorption (≤ 8 wt.%, see chapter 2). On the other hand the interaction between acetic acid and water may be quite high due to the hydrogen-bonding ability between the two components. Therefore, a strong influence of the faster permeating water molecules on the relatively slowly permeating acetic acid molecules may be expected. The higher the water flux (thin membranes) the more acetic acid will be dragged along by the water flux, and because the water flux is much higher than the acetic acid flux, the effect of the latter on the water flux will be negligible. By making the membrane thinner the flux of both components will increase, but due to coupling an extra flux increase of the slowest permeating component can be expected. In order to explain a decrease in selectivity as a function of membrane thickness due to flow coupling, transport relations are derived in terms of a friction model.

The transport equation for component i of a binary mixture permeating through a membrane can be expressed in terms of driving forces and friction [9]

- (Driving Force on i) = (Friction of j on i) + (Friction of membrane on i)

The following Maxwell-Stefan equations can be derived for a binary mixture of components i and j permeating through a polymer

$$\frac{1}{RT}\frac{d(\mu_i)}{dz} = \frac{(v_j - v_i)}{D_{ij}} - \frac{v_i}{D_{im}} \tag{1a}$$

$$\frac{1}{RT}\frac{d(\mu_j)}{dz} = \frac{(v_i - v_j)}{D_{ji}} - \frac{v_j}{D_{jm}} \tag{1b}$$

Substitution of the chemical potentials by the activities results in the relations

$$\frac{d(\ln a_i)}{dz} = \frac{x_j(v_j - v_i)}{D_{ij}} - \frac{(x_m v_i)}{D_{im}} \tag{2a}$$

$$\frac{d(\ln a_j)}{dz} = \frac{x_i(v_i - v_j)}{D_{ji}} - \frac{(x_m v_j)}{D_{jm}} \tag{2b}$$

With $J_i = v_i\overline{C_i}$, $J_j = v_j\overline{C_j}$, $\frac{x_m}{D_{im}} = \frac{1}{D'_{im}}$ and $\frac{x_m}{D_{jm}} = \frac{1}{D'_{jm}}$

the component fluxes can be expressed as

$$J_i = \left[\frac{(\overline{C}_i D_{ij} D'_{im})}{a_i(x_j D'_{im} + D_{ij})}\right]\left[\frac{(J_j a_i x_j)}{(\overline{C}_j D_{ij})} - \frac{da_i}{dz}\right] \qquad (3a)$$

$$J_j = \left[\frac{(\overline{C}_j D_{ji} D'_{jm})}{a_j(x_i D'_{jm} + D_{ji})}\right]\left[\frac{(J_i a_j x_i)}{(\overline{C}_i D_{ji})} - \frac{da_j}{dz}\right] \qquad (3b)$$

These relations are similar to the relations derived by Kedem [10].

$$\overline{P}_i = \left[\frac{(\overline{C}_i D_{ij} D'_{im})}{(x_j D'_{im} + D_{ij})}\right] \; ; \; \overline{P}_j = \left[\frac{(\overline{C}_j D_{ji} D'_{jm})}{(x_i D'_{jm} + D_{ji})}\right]$$

$\overline{P}_i$ and $\overline{P}_j$ represent the permeability coefficient of component i and j, respectively.

$\overline{Q} = \frac{x_j}{(\overline{C}_j D_{ij})} = \frac{x_i}{(\overline{C}_i D_{ji})}$ represents the mutual drag coefficient.

relations (3a) and (3b) can now be expressed as:

$$J_i = -\frac{\overline{P}_i}{a_i}\frac{d(a_i)}{dz} + \overline{Q}\,\overline{P}_i\, J_j \qquad (4a)$$

$$J_j = -\frac{\overline{P}_j}{a_j}\frac{d(a_j)}{dz} + \overline{Q}\,\overline{P}_j\, J_i \qquad (4b)$$

There is no direct relation between $\overline{P}$ and the membrane thickness nor between $\overline{Q}$ and the membrane thickness.

Assuming constant coefficients integration of relations (4a) and (4b) gives:

$$J_i = \frac{\overline{P}_i}{\Delta z} \ln\left(\frac{a'_i}{a''_i}\right) + \overline{Q}\,\overline{P}_i\, J_j \tag{5a}$$

$$J_j = \frac{\overline{P}_j}{\Delta z} \ln\left(\frac{a'_j}{a''_j}\right) + \overline{Q}\,\overline{P}_j\, J_i \tag{5b}$$

In the case of highly selective membranes, $J_i >> J_j$ and therefore the last term on the right hand side of relation (5a) can be neglected. By changing the membrane thickness $\overline{P}$, $\overline{Q}$ and the driving force remain constant. To study the influence of flow coupling on the component fluxes as a function of the membrane thickness, relations (5a) and (5b) can be simplified by

$$J_i = \frac{C_1}{\Delta z} \tag{6a}$$

$$J_j = \frac{C_2}{\Delta z} + C_3 J_i = \frac{C_2}{\Delta z} + C_3 \frac{C_1}{\Delta z} \tag{6b}$$

From relations (6a) and (6b) it can be concluded that the flux of the faster permeating component i influences the flux of j when C_3 is relatively large, which means a large mutual interaction between component i and j.

Furthermore, it can be concluded that both component fluxes are proportionally related to the reciprocal membrane thickness and that the ratio of the component fluxes is constant and independent of the membrane thickness. Therefore, flow coupling cannot explain the decrease in selectivity using thin membranes, unless $\overline{Q}$ and/or $\overline{P}$ are dependent on the membrane thickness.

That this is not unrealistic might be concluded from the observations by Park [11], Mandelkern et al. [12] and Ware and Cohen [13]. They observed independently that at non-equilibrium conditions thin films absorb more penetrant molecules per surface area than thick films. Ware and Cohen also found that this occurs below a limiting thickness. This indicates that during pervaporation at steady state *the degree of swelling of thin membranes might be larger than of thick films*. If this is true the average concentration $\overline{C}_i$ will be higher for thin films below a limiting thickness, which results in variable values for $\overline{Q}$ and $\overline{P}$ as a function of the membrane thickness.

Sorption Resistance

Kim and Kammermeyer [14] observed a sorption resistance at the liquid-polymer interface for permeation of a single component through thin films. This resistance increases with decreasing membrane thickness and results in a lower surface concentration of the permeant compared to the free equilibrium sorption concentration. Due to a reduced driving force a lower flux is obtained.

In the case of acetic acid/water mixtures only a sorption resistance for water might explain a decrease in selectivity. However, water shows a perfect Fickian behaviour with decreasing membrane thickness, while the acetic acid flux increases more than proportionally. Therefore, a sorption resistance can not explain the decrease in selectivity in the case of acetic acid/water separation using thin films.

Sorption Induced Defects

The additional increase of the acetic acid flux with decreasing membrane thickness might of course be the result of small defects in the membrane. However, directly after membrane preparation only in the case of thin (± 4 μm) PVC membranes defects were present large enough to affect the selectivity. This can be concluded from gas separation experiments and atomic force microscopy results. In the case of PSF and PAN we conclude that defects must then be introduced during pervaporation.

Crazes and cracks can be formed in polymeric materials once a critical strain ε_i has been reached. The formation of crazes is enhanced in a chemically active environment due to plasticization of the material and the reduction of the surface energy of the craze fibrils, and in the end might even result in material failure (cracks). The crazing agent acts through its presence within the polymer matrix. By increasing the chain mobility (lowering T_g) the penetrant facilitates the primary and secondary steps of craze initiation: nucleation and stabilization of a craze. It causes the lowering of critical strain and stress in polymers such as polystyrene, polysulfone, polyvinylchloride, polyphenyleneoxide or polycarbonate [15]. Polysulfone e.g. shows a reduction of critical strain by more than a factor 10, from 2.5 % in air to ± 0.2 % in organic liquids with a solubility parameter between 9 and 12 [16]. Therefore, craze initiation can be defined as the localized collective dilatational reorganization of stiff chain segments accompanied by matrix break-up [15].

Material failure has already been observed for relatively thick PSF and polyethersulfone membranes (chapter 2) when failure occurred at the place where the O-ring is pressing on the membrane.

Hopfenberg [17] observed solvent induced crazes at the swelling front when he examined cross sections of polystyrene samples, which had been immersed in n-alkane. During the beginning of the sorption process large concentration differences can be observed across the membrane resulting in stress formation transverse to the direction of diffusion [18] (see figure 7).

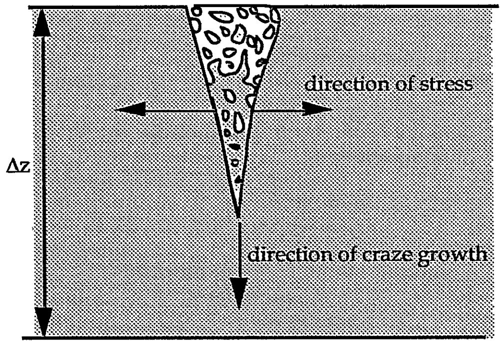


Figure 7 *Schematic representation of a craze in a polymer film*

The swollen region generates tensile forces on the unswollen, glassy region, whereas the glassy region causes compressive forces on the swollen region.

Comyn [19] describes examples of the formation of microcavities due to environmental stress-cracking and Drioli et al [20] describe permeability experiments carried out with polystyrene, polycarbonate and acrylonitrile-butadiene-styrene membranes with and without the presence of crazes (generated by applying a high pressure on the polymer film). They observed permeability through these crazes as well as a reduction of crazes by the presence of glass beads in the polymer and upon approaching the glass transition temperature of the polymer. The disappearance of crazes at the glass transition temperature has also been observed by Nicolais and Di Benedetto [21] and by Salee [22].

In the case of pervaporation large concentration differences across the membrane are present, which might result in the presence of stresses analogous to the non-equilibrium stage of sorption. Due to these stresses and the plasticizing effect of the acetic acid/water solution crazes might be initiated and grow in the direction of diffusion as long as there is enough liquid present at the tip of the craze.

Due to the low pressure at the permeate side and the relatively unswollen state of the membrane the craze will stop growing at that distance in the membrane where the concentration of the permeating liquid becomes too low (decreased plasticization). In other words, the layer at the permeate side which contains a liquid concentration lower than a critical concentration C* is responsible for blocking of craze growth. In case the mechanical strength of this layer is too small crazes may break through and could result in defects of the membrane which covers the whole membrane thickness.

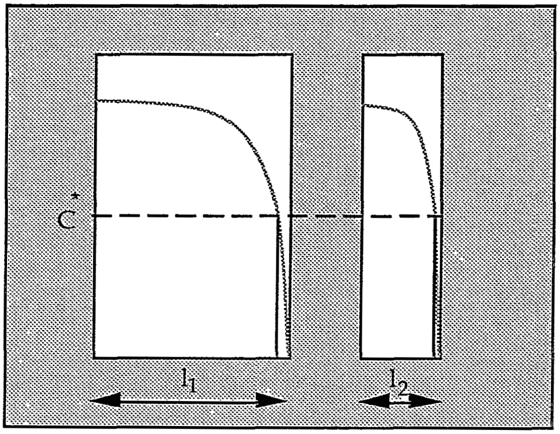


Figure 8 *Schematic representation of the same concentration profile of a single component in two membranes of different thicknesses*

In figure 8 a concentration profile is given for a thick and for a thin membrane. According to the solution-diffusion theory the concentration as a function of the relative distance in the membrane should be the same for both membranes. From this figure it can be concluded that the layer with a liquid concentration lower than C* and responsible for blocking of craze growth is thinner in the case of a thin membrane compared to that in a thick membrane. In order to explain (below a certain membrane thickness) the strong flux increase of acetic acid with decreasing membrane thickness one might conclude that a limiting thickness of the relatively unswollen layer is required to stop the craze from growing. Below this thickness crazes might break through due to a lack of mechanical stability. The thinner the membrane the more crazes will break through, and the higher the contribution of craze flux to the total membrane flux will be.

The craze flux is very small compared to the total membrane flux and will increase both component fluxes. Because the acetic acid flux for pervaporation is so small in comparison with the water flux the addition of a small but almost equal craze flux for both components to the pervaporation flux will have a larger influence on the acetic acid flux than on the water flux. The size of these crazes can be as large as 200-3000 Å, which has been observed for polystyrene [20].

From the results presented in figures 2 to 5 it was concluded that the effect of selectivity decrease for PVC is much less than for PSF and PAN. Since the pervaporation experiments have been carried out at 80 °C and the glass transition temperatures of PVC, PAN and PSF according to literature [23] are 87, 120 and 190 °C respectively, this is in good agreement with the observations of craze reduction upon approaching the glass transition temperature.

Let us assume that crazes are formed and that they result in defects which can be compared with capillary holes. In the case of pervaporation the flux through capillaries can be described by Knudsen flow. The flux for component i can than be expressed by

$$J_{i,\text{total}}(z) = J_{i,\text{pervap.}}(z) + J_{i,\text{ Knudsen}}(z) \tag{7}$$

With:

$$J_{i,\text{ Knudsen}}(z) = 0 \qquad \text{for } z \geq 20\ \mu\text{m} \tag{8}$$

$$J_{i,\text{ Knudsen}}(z) = \frac{1}{3} d_p \cdot \sqrt{\frac{8}{\pi R T M_i}} \cdot n \cdot \left(\frac{A_p}{A_m}\right) \cdot \frac{d(p_i)}{dz} \tag{9}$$

$$\text{for } z < 20\ \mu\text{m}$$

The flux contribution due to pervaporation can be calculated from the flux obtained for a membrane with a thickness of 20 µm using the relation

$$\frac{J_{i,\mathrm{pervap.}}(z)}{J_{i,\ \mathrm{total}}(20\mu\mathrm{m})} = \frac{1/z}{1/20} = \frac{20}{z} \qquad (10)$$

For membranes thinner than 20 µm the total acetic acid flux and water flux were measured (see figures 3 to 5) and the pervaporation fluxes were calculated with the help of equation (10). The flux contribution due to Knudsen flow can now be calculated from the experimentally obtained flux by choosing a fixed value for the pore diameter d_{pore} and taking the number of pores n as a fitting parameter. This was done for the acetic acid flux with d_{pore} = 0.3 µm (this pore size is a chosen value). With the number of pores found by fitting the acetic acid flux and a pore diameter of 0.3 µm also the total water flux can be calculated and compared with the total water flux that was measured. In order to meet the measured acetic acid flux the number of pores found for the *thinnest* membranes should be 818 per cm^2 for a 3.5 µm PAN membrane, 133 per cm^2 for a 9 µm PSF membrane and 58 per cm^2 for a 3 µm PVC membrane. If the pore size is fixed at a smaller value the number of pores increases. These calculations only show whether the pervaporation flux of water as a function of the reciprocal membrane thickness will be influenced by the extra contribution of transport through the number of capillaries calculated from the fitting procedure.

The measured water fluxes (squares) and the calculated water fluxes from the model (dashed lines) are plotted together in figure 9. From this figure it can be concluded that the calculated water fluxes show a linear relationship with the reciprocal membrane thickness and that they seem to be in good agreement with the experimentally obtained values. The extra flux through the capillaries is so small that it does not influence the pervaporation flux of water.

A calculated decrease in selectivity with decreasing membrane thickness could also be obtained from the water/acetic acid ratio in the permeates calculated by the model. Only for membranes thinner than 5-6 µm the calculated values start to deviate a little, although not systematically, from the experimental values. At these thicknesses the contribution of Knudsen flow is relatively large, from which it might also be concluded that a different kind of flow other than Knudsen flow takes place through crazes (e.g. surface diffusion).

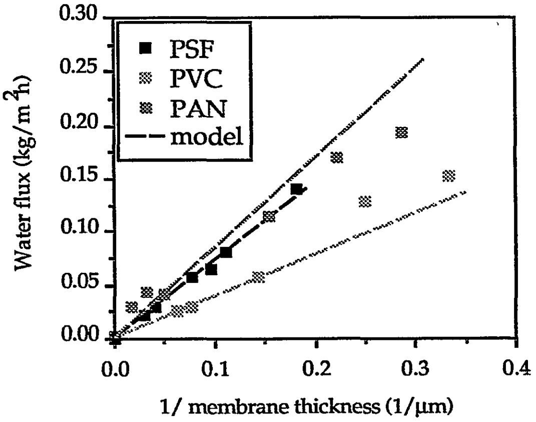


Figure 9 *Experimentally obtained water fluxes (squares) and calculated water fluxes (dashed lines) as a function of the reciprocal membrane thickness for PSF, PVC and PAN*

To gain more evidence for the existence of solvent induced defects in thin membranes, pervaporation experiments have to be carried out at variable feed pressures. The pervaporation flux will hardly be influenced, but the flux due to Knudsen flow will.

CONCLUSIONS

From gas separation and pervaporation experiments with PSF, PVC and PAN membranes of variable thicknesses it can be concluded that gas separation selectivity is independent of the membrane thickness as is described by the solution-diffusion theory and that in the case of pervaporation the selectivity decreases with decreasing membrane thickness below a limiting thickness (~ 20 µm).

The decrease of selectivity as a function of the membrane thickness could not be explained by differences in polymer morphology, nor by sorption resistances.

This dependance of selectivity on the membrane thickness was analysed with respect to flow coupling, but again could not be explained from this effect. Only if the mutual drag coefficient Q or the permeability coefficient P increase with decreasing membrane thickness a selectivity decrease can be explained.

The formation of defects during pervaporation due to solvent induced craze formation was discussed. Transport through these defects could be well described by Knudsen flow. By fitting the number of pores as a function of the membrane thickness the calculated water fluxes are in good agreement with the experimentally obtained values. Only at very small thicknesses the calculated values deviate from the experimental ones.

Although the phenomenon of decreasing selectivity in pervaporation upon decreasing membrane thickness is not yet completely understood, its appearance has been clearly proven.

LIST OF SYMBOLS

Symbol		**units**
a	activity	
a', a"	activity feed, activity permeate	
A	surface area	m^2
C	concentration	mol/m^3
d	diameter	m
D	diffusivity	m^2/s
J	flux	mol/s
M	molecular weight	kg/mol
n	number of pores	
p	pressure	N/m^2
Q	mutual drag coefficient	m.s/mol
R	gas constant	J/mol K
P	permeability coefficient	mol/m s
T	temperature	K
v	velocity	m/s
x	mol fraction	
z	thickness, distance	m
μ	chemical potential	J/mol

indices

av	average	m	membrane
i,j	components i and j	p	pore

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5

POLYVINYLCHLORIDE/POLYACRYLONITRILE COMPOSITE MEMBRANES FOR THE DEHYDRATION OF ACETIC ACID

INTRODUCTION

Polyvinylchloride (PVC) appeared to be a suitable commercially available polymer to serve as a membrane material for the dehydration of acetic acid by pervaporation as has been described in chapter 2.

Once a satisfactorily selective polymer has been found a membrane has to be developed with a separating layer thin enough to obtain a maximum permeate flux. These required fluxes dictate a separating layer smaller than 1-2 μm.

Homogeneous dense membranes of 1-2 μm thickness do not posses enough mechanical stability and need to be supported by a porous layer having a negligible contribution to the overall transport resistance, but a sufficient mechanical strength. Two types of membranes can be distinguished, viz. i) integrally skinned membranes, where toplayer and support layer originate from the same material and ii) composite membranes, where toplayer and support layer consist of different materials.

Integrally skinned membranes can be obtained e.g. by casting a polymer solution followed by an evaporation step before the polymer solution is coagulated in a nonsolvent bath. Due to evaporation of the solvent the surface concentration becomes high enough resulting in a thin dense layer after phase inversion, while directly under the toplayer, where the polymer concentration is much lower, a porous layer will be formed. These techniques to obtain an integrally skinned membrane has been developed by Pinnau (toplayers of 300-1000 Å) [1,2] and by van 't Hof (toplayers of about 1μm) [3,4]. The method developed by van 't Hof, the so called "dual bath method" has been discussed in detail in chapter 3.

The first commercial pervaporation membrane is the composite membrane developed by GFT [5] for the dehydration of alcohols. This membrane consists of a crosslinked polyvinylalcohol (PVA) toplayer and a polyacrylonitrile (PAN) support layer. It combines high selectivity with a high flux.

In the development of a composite membrane the structure of the support layer is very important. To avoid capillary condensation inside the porous support the pores may not be too narrow. With the Kelvin relation (eq. 1) it can be calculated at what pressures capillary condensation occurs as a function of the pore radius.

$$\ln\left(\frac{P}{P_s}\right)=\left(\frac{-\gamma\, V_m}{RT}\right)\cos\theta.\frac{1}{r} \qquad (1)$$

On the other hand when the pore diameters are too large, problems might occur in achieving a thin defect-free coating layer (toplayer). A schematic representation of a composite membrane is given in figure 1.

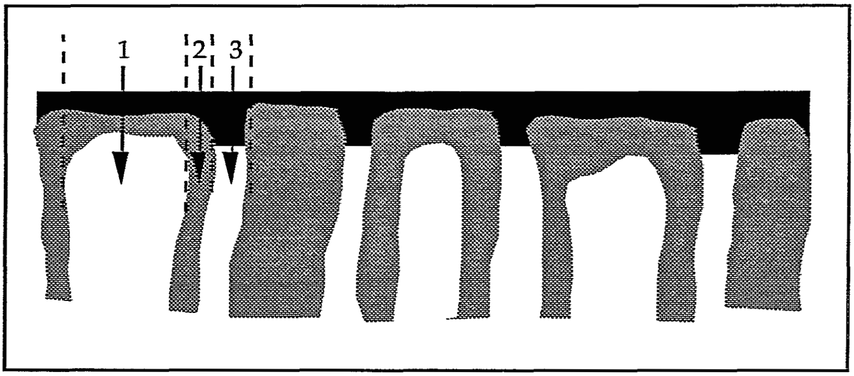

Figure 1 *Schematic representation of a composite membrane showing three different permeating regions*

Three different transport regions can be distinguished, each with a specific resistance, viz. the resistance belonging to region 1 which consists of a thin toplayer and a thin layer of the support material in series, the resistance beloning to region 2, which consists of a thin toplayer and a thick layer of the support material in series and the resistance belonging to region 3, which only consists of the thin toplayer. Because resistance (2) is much larger compared to the other two resistances (1) and (3) transport will not occur through region (2).

Ideal support layers for composite membranes must have a relatively high surface porosity and the separation properties of these composite membranes will be mainly determined by the toplayer, unless the toplayer material penetrates in the pores of the sublayer to a depth which results in a much higher resistance (3) compared to resistance (1).

A relatively low surface porosity results in a larger contribution of the support material to the separation properties of the composite membrane. This principle has been applied successfully by Henis and Tripodi [6] in the development of the Monsanto Prism® membrane for hydrogen recovery; they plugged the pores of a polysulfone hollow fiber membrane (having a relatively low surface porosity) with silicon rubber resulting in a membrane with the intrinsic selectivity belonging to polysulfone.

To prepare a composite membrane with a defect-free toplayer e.g. by dip-coating or solution casting techniques the coating solution has to show good wetting properties on the support material. Furthermore, the solvent for the toplayer material may not attack the structure of the support layer.

In this chapter the development of a composite membrane will be studied, using highly selective PVC as toplayer material and PAN as support material (which also by itself has a high selectivity).

EXPERIMENTAL

Materials

Polyacrylonitrile (PAN-7A) was obtained from Du Pont, Polyvinylchloride (PVC, high Mw) from Aldrich, Polyester nonwoven (FO 2401) from Freudenberg, and PAN support layers from GFT.

Tetrahydrofuran (THF) was used as a solvent for PVC and N,N-dimethylformamide (DMF) was used as a solvent for PAN, both were of analytical grade and were obtained from Merck.

Membrane Preparation

PAN support layers were prepared by a phase inversion process. 20 to 27.5 wt.% PAN was dissolved in DMF and filtered over a 0.5 μm metal filter. The filtered PAN solution was casted on a nonwoven support by a casting machine (figure 2) and coagulated in water at various temperatures. After rinsing with water for at least 24 hours the casted PAN support layer was cut into pieces of 25x20 cm, immersed into an ethanol bath for 4 hours followed by immersion into a hexane bath for another 4 hours. Then the support layers were dried in air for at least two days before they were coated.

The PAN support layers (both prepared in our lab as well as obtained from GFT) were coated with a 3-10 wt.% PVC solution in THF, either by dip-coating or by solution casting. Before dip-coating the 25x20 cm PAN support layers were glued at the edges with the nonwoven side facing the glass plate, so that no PVC could reach the back side of the support layer during immersion into the PVC solution. The PAN support layer glued on the glass plate was put into a glass box in a vertical position. The box was then filled with a PVC solution and emptied after waiting for 5-10 minutes, by opening a small tap at the bottom of the box. The membrane was dried at room temperature for at least 1 day. In this way composite membranes with a dense PVC toplayer on a porous PAN support layer were prepared. Dip-coating results in thinner toplayers than solution casting.

Also dense PVC/PAN bi-layers were prepared by first solution casting of a 15 wt.% PAN solution on a glass plate followed by evaporation of the solvent in a nitrogen atmosphere. After the solvent had evaporated completely a 5-10 wt.% PVC solution in THF was casted on top of the dense homogeneous PAN layer. Finally the solvent was allowed to evaporate in a nitrogen atmosphere and the bi-layer membranes were dried in a vacuum oven at 80 °C for 1 week.

Pervaporation

Pervaporation experiments were carried out using a set-up as described in chapter 2 (figure 1). The permeate side was maintained at a pressure of 0.1-0.5 mmHg by a Crompton Parkinson vacuum pump. The pressure was measured by an Edwards pirani meter. Permeate samples were taken every hour, during 8 hours. Steady-state was normally observed after 2-3 hours. The permeate was analysed using a Varian 3700 Gas Chromatograph filled with a Poropack Q column at a temperature of 190 °C.

Support Permeability

The air permeability of all the support layers were measured by a Coulter Porometer II.

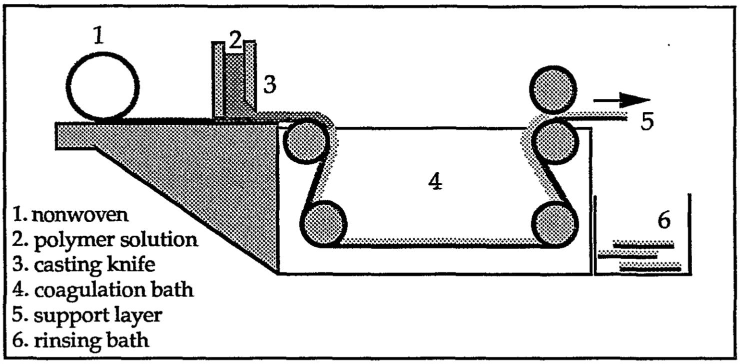

Figure 2 *Schematic representation of a membrane casting machine*

Toplayer Thickness

The toplayer thickness of the composite membranes were determined from Scanning Electron Microscopy (SEM) pictures. Membrane samples were immersed in a 50/50 vol.% water/ethanol mixture, frozen in liquid nitrogen followed by breaking. After drying, the samples were provided with a thin gold layer and studied by SEM. A SEM picture of a typical PVC/PAN composite membrane is given in figure 3. The PAN support layers contain large macrovoids starting from the nonwoven side and ending at a distance of about 3 µm from the porous PAN toplayer. A dense 0.3 µm thin PVC toplayer can be distinguished as the white line on top of the support layer.

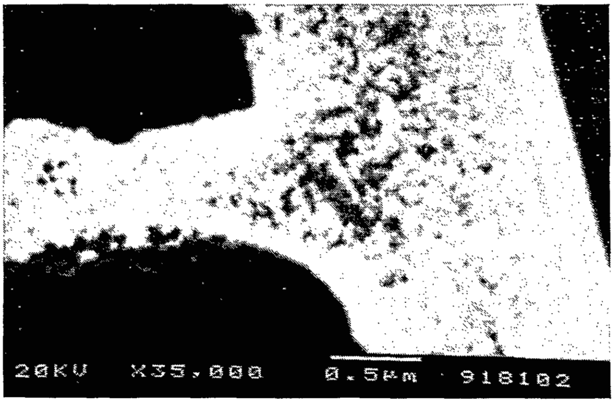

Figure 3 *Cross section of a PVC/PAN composite membrane; the thin white line is the PVC toplayer (0.3 µm) and the the grey layer with the macrovoids is the porous PAN support layer*

RESULTS AND DISCUSSION

Dense (bi-layer) Membranes

From our study on membrane thickness (chapter 4) it was observed that the selectivity of PVC films drops dramatically when the membrane thickness is decreased below a certain value (~10 µm). Therefore, a relatively low selectivity can be expected for a composite membrane which consists of a highly porous PAN support layer covered by a thin PVC layer less than 1 µm thick; in this case selectivity and flux will be mainly determined by the PVC layer. A possible contribution of the support material to the selectivity (through the effect of the transport pathway 1 in figure 1) can be altered by varying the porosity of the support layer.

To study the influence of the support material dense bi-layer membranes of PVC on PAN were prepared by solution casting of a PVC layer on top of a dense homogeneous PAN layer. Dense bi-layer membranes with different thicknesses were prepared and measured for the dehydration of acetic acid by pervaporation. The results of these measurements are represented in table 1. From this table it can be concluded that these bi-layer membranes are extremely selective compared to dense PVC single-layers of comparable thickness, especially for the dehydration of 98 wt.% acetic acid.

Table 1 *Selectivity and flux of dense PVC/PAN bi-layer membranes of variable total thickness for the dehydration of 80 wt.% and 98 wt.% acetic acid at 80 °C.*

PVC thickness (µm)	PAN thickness (µm)	Feed comp. (wt.% H_2O)	Permeate comp. (wt.% H_2O)	α	Flux (kg/m^{2}h)
2	11	20.00	99.90	3996	0.023
4.5	4.5	19.90	99.92	5027	0.035
3	3	21.10	99.00	370	0.064
1	2	21.20	98.90	334	0.099
2	11	2.00	84.80	273	0.005
4.5	4.5	2.10	99.30	6613	0.016
3	3	1.90	90.20	475	0.026
1	2	1.90	91.20	535	0.037

In case of PVC/PAN bi-layers the selectivity seems to decrease with decreasing membrane thickness, which has also been observed for PVC, PAN and PSF single-layer membranes (see chapter 4), but even a bi-layer membrane of 3 µm total thickness shows a higher selectivity at 98 wt.% acetic acid than a 20 µm PVC or PAN single-layer membrane (see tables 3 and 4). Due to the presence of the PVC layer the degree of sorption in PAN at the PVC/PAN interface will be much lower compared to the equilibrium sorption value of the feed in PAN and this might therefore reduce craze formation in the PAN layer, resulting in a selectivity of bi-layer membranes being less dependent on the layer thickness compared to PVC and PAN as a single-layer membrane.

The selectivity and flux of a dense PVC/PAN bi-layer membrane as a function of the feed composition is represented in table 2.

Table 2 *Selectivity and flux of a 9 µm dense PVC/PAN bi-layer membrane as a function of the feed composition for the dehydration of acetic acid by pervaporation at 80 °C.*

PVC thickness (µm)	PAN thickness (µm)	Feed comp. (wt.% H_2O)	Permeate comp. (wt.% H_2O)	α	Flux (kg/m^{2}h)
4.5	4.5	50.20	99.85	671	0.028
4.5	4.5	40.20	99.80	742	0.029
4.5	4.5	29.50	99.90	2387	0.030
4.5	4.5	19.90	99.92	5027	0.035
4.5	4.5	2.10	99.30	6613	0.016

The selectivity and flux values of a homogeneous PVC single-layer and a homogeneous PAN single-layer membrane as a function of the feed composition are represented in tables 3 and 4, respectively.

Table 2 shows that the selectivity of the bi-layer membrane increases with an increasing concentration of acetic acid in the feed. This is due to the fact that acetic acid flux is almost independent of the feed composition up till 98 wt.% acetic acid. For PVC and PAN membranes separately the acetic acid flux and therefore the acetic acid content in the permeate increases rapidly going from 80 wt.% to 98 wt.% acetic acid in the feed,

Table 3 *Selectivity and flux of a 20 μm dense PVC single-layer membrane as a function of the feed composition for the dehydration of acetic acid by pervaporation at 80 °C.*

PVC thickness (μm)	Feed comp. (wt.% H_2O)	Permeate comp. (wt.% H_2O)	α	Flux (kg/m^2h)
20	49.20	99.54	223	0.0174
20	40.30	99.45	268	0.0168
20	29.50	99.30	339	0.0174
20	19.90	99.00	398	0.0192
20	9.80	96.30	240	0.0192
20	2.00	62.70	82	0.0232

Table 4 *Selectivity and flux of a 20 μm dense PAN single-layer membrane as a function of the feed composition for the dehydration of acetic acid by pervaporation at 80 °C.*

PAN thickness (μm)	Feed comp. (wt.% H_2O)	Permeate comp. (wt.% H_2O)	α	Flux (kg/m^2h)
20	49.70	99.92	1264	0.061
20	40.00	99.92	1874	0.076
20	29.70	99.91	2628	0.063
20	21.80	99.84	2238	0.040
20	10.90	99.60	2042	0.022
20	1.80	83.70	280	0.006

resulting in a decrease of the selectivity.

The experimentally measured pervaporation selectivity and component fluxes through dense PVC and PAN single-layers and dense PVC/PAN bi-layer membranes at different feed compositions and also the equilibrium sorption and sorption selectivity values for these membranes are represented in table 5.

Table 5 *Equilibrium sorption, sorption selectivity, acetic acid flux, water flux and pervaporation selectivity as a function of the feed composition for dense PVC and PAN single-layer membranes and dense PVC/PAN bi-layer membranes*

Membrane	Feed (acid/water) (wt.%)	Sorption (wt.%)	Sorption Selectivity (α^S(w/a))	Acetic acid flux (g/m^2h)	Water flux* (g/m^2h)	α perv.
PVC	00/100	0.8	1.0	-	4.4	-
PAN	00/100	12.4	1.0	-	101	-
PVC/PAN**	00/100	-	-	-	53	-
PVC	100/00	10.6	1.0	49	-	-
PAN	100/00	6.9	1.0	10	-	-
PVC/PAN	100/00	-	-	2.4	-	-
PVC	98/2	9.6	1.52	19	32	82
PAN	98/2	5.9	3.69	2	11	280
PVC/PAN	98/2	-	-	0.1	16	6613
PVC	80/20	3.6	0.71	0.4	42	398
PAN	80/20	6.4	1.06	0.1	89	2238
PVC/PAN	80/20	-	-	0.003	35	5027

* Fluxes normalized to a membrane thickness of 9 μm
** Consists of 4.5 μm PVC and 4.5 μm PAN

From table 5 it can be concluded that the water flux of the bi-layer membrane is always in-between the water flux of the single-layer PVC and PAN membranes, while the acetic acid flux of the bi-layer is always lower than the lowest flux of the two single-layer membranes (in this case PAN).

The sorption selectivity of PVC and PAN are for both materials close to 1 (see chapter 2). Therefore, the difference in driving force can be neglected in the case of equal feed compositions. The membrane with the highest degree of sorption should then have the highest flux, which is in agreement with the results represented in table 5.

Furthermore, a higher selectivity would be expected for the membrane with the lower degree of sorption. However, at a feed of 80/20 wt.% acetic acid/water the PAN membrane, showing a higher sorption value also exhibits a higher selectivity than PVC. In this case the PVC membrane did not show its intrinsic selectivity (α = 4750; mean selectivity α = ± 600), which is, in accordance with the expectation, higher than the intrinsic

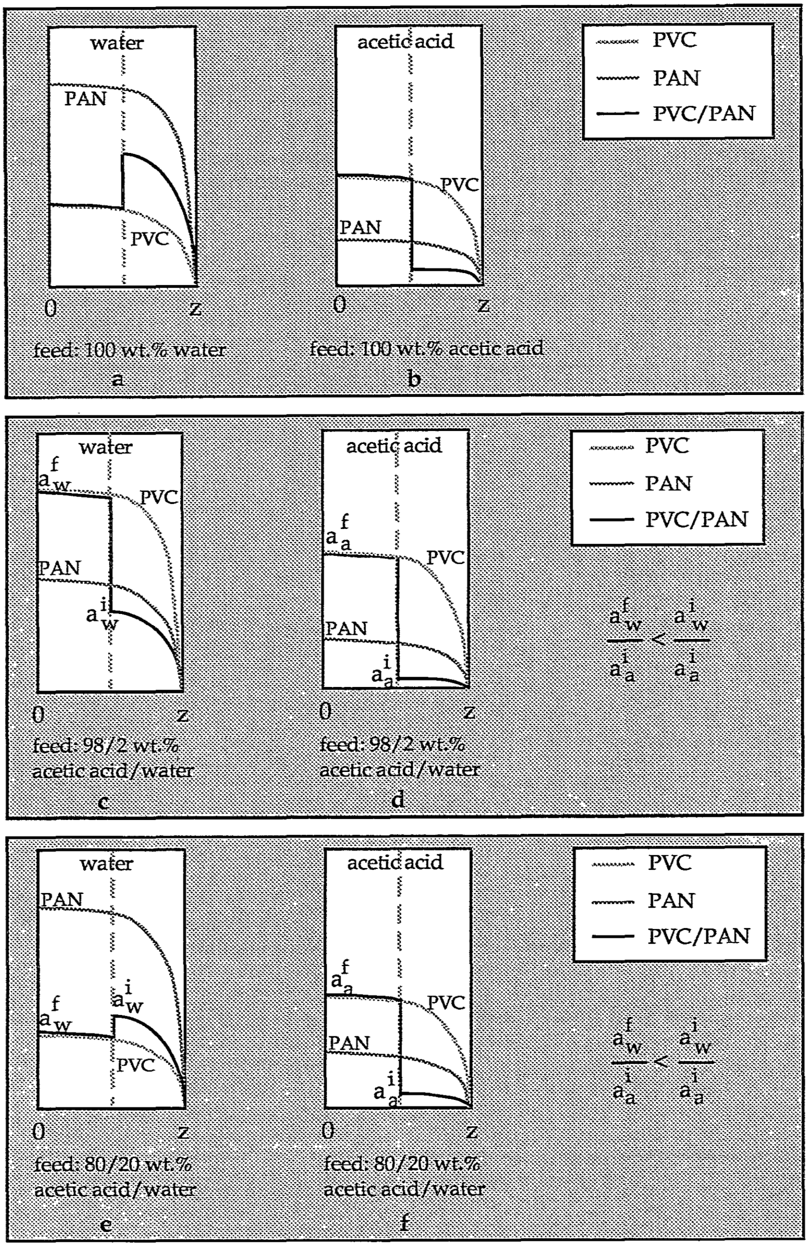

Figure 4 *Schematic representation of possible concentration profiles of water and acetic acid in dense PVC and PAN single-layer membranes and dense PVC/PAN bi-layer membranes during pervaporation using different feed compositions;(dashed line represents the PVC/PAN interface)*

selectivity of PAN ($\alpha = 2240$).

Due to the presence of the PVC layer the component concentration in PAN at the PVC/PAN interface will always be lower than the concentration in PAN in case of equilibrium sorption and the component activities at the PVC/PAN interface are also lower than the activities at the feed side. Together with the experimentally obtained component fluxes concentration profiles in PVC, PAN and PVC/PAN can be estimated. A schematic representation of possible concentration profiles of acetic acid and water at different feed compositions is given in figure 4 (dashed line represents the PVC/PAN interface).

In figure 4a, 4c and 4e the average water concentration in the bi-layer membrane is in-between the average water concentration of both single-layer membranes. The average acetic acid concentration is always lower than the average concentration in PAN, the less swollen of the two single-layers (figure 4b, 4d and 4f).

To verify this hypothesis the component concentrations have to be determined at the PVC/PAN interface and at a comparable distance in the PVC and PAN membranes. The "exponential 6-parameter model" of Brun [7] was used to determine the activities at the PVC/PAN interface. This model expresses the component flux ratio as

$$\frac{J_i}{J_j} = \frac{D_{i,0}K_j}{D_{j,0}K_i}\left[\frac{\exp(K_i\, S_i\, a_i^p) - \exp(K_i\, S_i\, a_i^f)}{\exp(K_j\, S_j\, a_j^p) - \exp(K_j\, S_j\, a_j^f)}\right] \tag{2}$$

With the activities a_i^p and a_j^p at the permeate side equal to zero and a relation for the activity a_j^f as a function of the activity a_i^f at the feed side, values for $\frac{D_{i,0}K_j}{D_{j,0}K_i}$, K_iS_i and K_jS_j can be determined by fitting relation (2) to the experimental values of J_i/J_j as a function of a_i^f. This has been done for homogeneous PAN and PVC membranes for the dehydration of acetic acid and has been worked out and described in the appendix following this chapter. One can see that the water flux/acetic acid flux ratio through homogeneous PAN and PVC membranes can be quite well described as a function of the water activity in the feed using this model.

Since, the flux ratio of a PVC/PAN bi-layer membrane is the same for the PVC layer as for the PAN layer the following relation can be derived

$$\frac{J_i}{J_j} = \left(\frac{D_{i,0}K_j}{D_{j,0}K_i} \left[\frac{\exp(K_i\,S_i\,a_i^p) - \exp(K_i\,S_i\,a_i^f)}{\exp(K_j\,S_j\,a_j^p) - \exp(K_j\,S_j\,a_j^f)} \right] \right)_{PVC}$$

$$= \left(\frac{D_{i,0}K_j}{D_{j,0}K_i} \left[\frac{\exp(K_i\,S_i\,a_i^p) - \exp(K_i\,S_i\,a_i^f)}{\exp(K_j\,S_j\,a_j^p) - \exp(K_j\,S_j\,a_j^f)} \right] \right)_{PAN} \qquad (3)$$

The activities of the components i and j at the PVC/PAN interface in PVC and PAN, respectively are the same. Considering the activities in PAN at the PAN permeate interface equal to zero relation (3) can be rearranged to

$$\left[\frac{D_{i,0}K_j}{D_{j,0}K_i} \right]_{PVC} \left[\frac{\exp((K_i\,S_i)_{PVC}\,a_i^{interf.}) - \exp((K_i\,S_i)_{PVC}\,a_i^f)}{\exp((K_j\,S_j)_{PVC}\,a_j^{interf.}) - \exp((K_j\,S_j)_{PVC}\,a_j^f)} \right] =$$

$$\left[\frac{D_{i,0}K_j}{D_{j,0}K_i} \right]_{PAN} \left[\frac{1 - \exp((K_i\,S_i)_{PAN}\,a_i^{interf.})}{1 - \exp((K_j\,S_j)_{PAN}\,a_j^{interf.})} \right] \qquad (4)$$

Using the values for $\frac{D_{i,0}K_j}{D_{j,0}K_i}$, K_iS_i and K_jS_j determined for the single-layer membranes of PVC and PAN (see appendix) the activities $a_i^{interf.}$ and $a_j^{interf.}$ at the PVC/PAN interface can be calculated.

Both these calculated activities appeared to be higher than the activities at the feed side. This must be due to the fact that the constants $\frac{D_{i,0}K_j}{D_{j,0}K_i}$, K_iS_i and K_jS_j of PAN in a bi-layer membrane are different compared to the constants of PAN as a single-layer membrane.

In the case of a single-layer membrane the relation which describes the acetic acid activity as a function of the water activity in the membrane at the feed side is completely determined by free equilibrium sorption, while in the case of a bi-layer membrane this relation is dependent on the layer at the feed side of the PAN layer. A different relation for the acetic acid activity as a function of the water activity results in different values for the constants. Unfortunately, this relation cannot be determined.

Composite Membranes

The influence of the PAN support layer was studied using GFT support layers as well as various support layers prepared by ourselves. These latter support layers are prepared by a phase inversion process using DMF as solvent and water as nonsolvent. In order to obtain different support layers mainly two parameters were varied, viz. the temperature of the coagulation bath and the polymer concentration of the dope. All the support layers were characterized by air permeability measurements and for some support layers the surface porosity and the average pore radius were determined. The results are represented in table 6.

Table 6 *Air permeability, average pore radius and surface porosity of differently prepared PAN support layers*

Supp. Nr.	PAN* (wt.%)	Temp. coag. bath (°C)	Air flow (l/cm^2 min**)	Average*** Pore Radius (nm)	Surface*** Porosity (m^2/m^2)
1	GFT 89008		0.394	5.1	1.22×10^{-4}
2	GFT 1411-B		1.026	9.2	4.34×10^{-4}
3	20	7.5	0.412	-	-
4	20	12.5	0.517	-	-
5	20	15.5	0.520	-	-
6	20	17.5	0.414	21.4	1.65×10^{-4}
7	25	18.0	0.096	10.1	6.24×10^{-5}
8	27.5	18.0	0.032	8.2	7.54×10^{-6}

* represents PAN concentration in the casting solution
** feed pressure: 2 bar
*** determined by Dr. G. Ellinghorst (GFT)

Changing the coagulation bath temperature from 7.5 to 17.5 °C did not have much influence on the porosity as can be concluded from the air permeability data represented in table 6. A large variety in surface porosity can be obtained by changing the polymer concentration in the casting dope; the porosity and the pore size decrease using higher polymer concentrations. Furthermore, it can be concluded that the pore diameter is smaller than 50 nm for all support layers. Therefore, no big problems would be expected with respect to coating. Once the pore radius is known the relative pressure P/P_S inside these pores can be calculated using the Kelvin relation (eq.1). With $\theta = 0$, which is generally accepted it can be calculated that the relative pressure $P/P_S = 0.97$ for a pore radius of 10 nm and $P/P_S = 0.98$ for a pore radius of 20 nm. From these calculations it can be concluded that the occurrence of capillary condensation in these pores is very unlikely.

After coating with a 5 wt.% PVC solution by solution casting or a dip-coating technique the composite membranes were measured for the dehydration of 80 wt.% and 98 wt.% acetic acid at 80 °C, respectively. The results of the coated GFT support layers are represented in table 7.

Using the permeability of a homogeneous PVC membrane it can be estimated that for a 1.2 µm thick PVC membrane (feed: 80/20 wt.% acetic acid/water) a flux of about $J = 0.308$ kg/m^{2}h is obtained. Comparing this value with the flux obtained for a composite membrane with the same toplayer thickness (1.2 µm) and a surface porosity of only 0.0122 % (see table 6), giving a flux of $J = 0.206$ kg/m^{2}h using the same feed composition, it can be concluded that almost all the permeant has passed a PVC/PAN bi-layer (see pathway 1 in figure 1) with a relatively small resistance in the PAN layer. It means that this PAN layer has to be very thin.

Table 7 *Selectivity and flux of PVC/PAN composite membranes for the dehydration of 80 wt.% and 98 wt.% acetic acid at 80 °C using GFT supports*

Supp. Nr.	GFT	Toplayer thickness (µm)	Feed comp. (wt.% H_2O)	Permeate comp. (wt.% H_2O)	α	Flux (kg/m^{2}h)
1*	89008	1.2	19.70	96.80	123	0.206
2*	1411-B	1.5	20.20	96.70	116	0.178
2**	1411-B	0.5	20.10	95.00	76	0.581
1*	89008	1.2	2.00	70.90	119	0.108
2*	1411-B	1.5	2.20	59.30	65	0.155
2**	1411-B	0.5	1.80	43.10	41	0.257

* solution casting;
** dip-coating

In chapter 4 it was concluded that the selectivity of PVC decreases with a decreasing membrane thickness. However, from experiments on dense PVC/PAN bi-layer membranes it can be concluded that these bi-layers, with a comparable thickness as a single PVC layer have a higher selectivity than a single-layer PVC membrane.Therefore, a higher surface porosity of the PAN support should result in a larger contribution to the overall membrane properties of PVC as being a single layer, which in that case should give lower selectivities due to surface and crazing effects. This is especially the case at higher acid concentrations in the feed, because then the difference in selectivity of a PVC/PAN and a PVC membrane becomes even larger; this is supported by the data represented in table 7, where support 1411-B has the larger surface porosity.

Changing the coagulation bath temperature and using a 20 wt.% PAN solution similar surface porosities were obtained as for the GFT 89008 support; only the pore radius is 4 times larger (see table 6). After dip-coating these supports with a 5 wt.% PVC solution the membranes were measured for pervaporation. The selectivity and flux for the dehydration of 80 wt.% and 98 wt.% acetic acid are represented in table 8.

Table 8 *The influence of the coagulation bath temperature (support layer) on selectivity and flux of PVC/PAN composite membranes for the dehydration of 80 wt.% and 98 wt.% acetic acid at 80 °C.*

Supp. Nr.	Temp. coag. bath (°C)	Toplayer thickness (µm)	Feed comp. (wt.% H_2O)	Permeate comp. (wt.% H_2O)	α	Flux (kg/m^{2}h)
3	7.5	0.5	19.90	97.70	171	0.624
4	12.5	0.5	19.60	97.80	182	0.565
5	15.5	0.5	19.70	97.70	173	0.581
6	17.5	0.8	20.30	96.60	112	0.527
3	7.5	0.5	1.90	66.90	104	0.252
4	12.5	0.5	1.50	60.40	100	0.227
5	15.5	0.5	1.40	47.40	63	0.270
6	17.5	0.8	1.40	51.20	74	0.277

According to the air flow data presented in table 6 the support layers show a small increase in porosity in the order 1 < 3 < 4 < 5. This difference does not affect the separation properties for the dehydration of 80 wt.% acetic acid as can be concluded from tables 7 and 8; the differences in porosity are too small.

However, using a feed of 98/2 wt.% acetic acid/water a significant increase of the water concentration in the permeate can be observed in the order 1 > 3 > 4 > 5. At this feed concentration the selectivity of a thin PVC layer becomes so low that even small differences in the surface porosity of the support do have a significant influence on the selectivity of the composite membrane. The influence on flux is negligible.

Anyhow, it should be noticed that the composite membranes with support layer numbers 3, 4 and 5 are highly selective in the dehydration of 80 wt.% acetic acid and in addition have high fluxes as well. The selectivity at 98 wt.% acetic acid is still too low, although the flux is sufficiently high. By decreasing the surface porosity of the support layer the selectivity may be improved.

Table 9 *The influence of the PAN concentration in the casting solution on selectivity and flux of PVC/PAN composite membranes for the dehydration of 80 wt.% and 98 wt.% acetic acid at 80 °C.*

Supp. Nr.	PAN* (wt.%)	Toplayer thickness (µm)	Feed comp. (wt.% H_2O)	Permeate comp. (wt.% H_2O)	α	Flux (kg/m^{2}h)
6	20	0.8	20.30	96.60	112	0.527
7	25	1.0	20.60	97.90	180	0.364
7	25	0.3	20.40	97.90	182	0.742
8	27.5	1.0	20.75	97.30	138	0.392
8	27.5	0.5	20.20	98.58	274	0.558
6	20	0.8	1.40	51.20	74	0.277
7	25	1.0	1.50	82.90	318	0.126
7	25	0.3	2.00	80.80	206	0.153
8	27.5	1.0	1.65	79.00	224	0.088
8	27.5	0.5	1.93	83.70	261	0.140

* represents PAN concentration in the casting solution

A successful decrease of the surface porosity was achieved by increasing the polymer concentration of the casting solution (see table 6). After dip-coating with a 3-5 wt.% PVC solution these membranes gave the following selectivity and flux values for the dehydration of acetic acid (see table 9).

From table 9 it can be concluded that a further decrease of the porosity results in higher selectivities at relatively high concentrations of acetic acid in the feed. At a concentration of 98 wt.% acetic acid in the feed the selectivity of the composite membrane increases spectacularly when the porosity of the support layer decreases. The fact that the selectivity increases using higher concentrations of acetic acid in the feed proves clearly that the support layer does contribute to the selectivity of the composite membrane (see table 2). The fluxes of these membranes decrease with decreasing porosity, but are still acceptable.

CONCLUSIONS

Extremely high selectivities can be obtained for the dehydration of highly concentrated acetic acid mixtures using a bi-layer membrane consisting of a dense PVC layer on top of a dense PAN layer. However, the fluxes are low as expected.

For composite membranes with a porous support layer of PAN coated with a thin PVC layer two different regions can be distinguished where transport takes place, viz. a region which consists of a PVC/PAN bi-layer and a region which consists of a PVC single-layer. Each of these regions has a characteristic resistance. Due to the fact that the bi-layer shows higher selectivities than homogeneous PVC single-layers of the same total thickness highly selective composite membranes can be developed by decreasing the surface porosity of the support.

LIST OF SYMBOLS

		unity
a	activity	-
A	plasticizing constant	-
C	concentration	mol/m^3
D	diffusion coefficient in membrane	m^2/s
D_0	diffusion coefficient at infinite dilution	

	of the permeant in the membrane	m^2/s
γ	interfacial tension	N/m
J	flux	kg/m^2h
K	intermediate constant of the model	-
P	vapour pressure	N/m^2
P_s	saturation pressure	N/m^2
r	pore radius	m
R	gas constant	J/mol K
S	sorption coefficient	mol/m^3
T	temperature	K
θ	contact angle	°
V_m	molar volume	m^3/mol
z	membrane thickness, distance	m

Subscripts		*Superscript*	
a	acetic acid	interf.	interface
i	component i	i	interface
j	component j	f	feed
w	water	p	permeate

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Appendix to Chapter 5

The "exponential 6-parameter model" of Brun [A.1] applied to the separation of acetic acid/water mixtures using PVC and PAN membranes

According to Fick the component fluxes for a binary mixture through a membrane can be described by the following relation

$$J_i = -D(c)_i \frac{d(C_i)}{dz} \tag{A1}$$

where D_i is a function of the component concentration. For both components i and j the diffusion coefficient can be expressed by

$$D_i = D_{i,0} \exp(A_{ii}\, C_i + A_{ij}\, C_j) \tag{A2a}$$

$$D_j = D_{j,0} \exp(A_{ji}\, C_i + A_{jj}\, C_j) \tag{A2b}$$

The molar flux ratio J_i/J_j is constant across the whole membrane and can now be expressed by

$$\frac{J_i}{J_j} = \frac{D_{i,0} \exp(K_i\, C_i).dC_i}{D_{j,0} \exp(K_j\, C_j).dC_j} \tag{A3}$$

with:

$$K_i = A_{ii} - A_{ji} \tag{A4a}$$

$$K_j = A_{jj} - A_{ij} \tag{A4b}$$

Integrating across the membrane results in the following expression for the component flux ratio

$$\frac{J_i}{J_j} = \frac{D_{i,0}K_j}{D_{j,0}K_i}\left[\frac{\exp(K_i\,\overline{C_i^p}) - \exp(K_i\,\overline{C_i^f})}{\exp(K_j\,\overline{C_j^p}) - \exp(K_j\,\overline{C_j^f})}\right] \tag{A5}$$

The concentration can be written in terms of activity using the following relation

$$C = S.a \qquad \text{(A6)}$$

relation (A5) then becomes

$$\frac{J_i}{J_j} = \frac{D_{i,0}K_j}{D_{j,0}K_i}\left[\frac{\exp(K_i\, S_i\, a_i^p) - \exp(K_i\, S_i\, a_i^f)}{\exp(K_j\, S_j\, a_j^p) - \exp(K_j\, S_j\, a_j^f)}\right] \qquad \text{(A7)}$$

By the following substitutions

$$m_1 = \frac{D_{i,0}K_j}{D_{j,0}K_i} \qquad \text{(A8)}$$

$$m_2 = K_iS_i \qquad \text{(A9)}$$

$$m_3 = K_jS_j \qquad \text{(A10)}$$

relation (A7) is simplified and becomes now

$$\frac{J_i}{J_j} = m_1 \cdot \left[\frac{\exp(m_2\, a_i^p) - \exp(m_2\, a_i^f)}{\exp(m_3\, a_i^p) - \exp(m_3\, a_i^f)}\right] \qquad \text{(A11)}$$

If the activities at the permeate side are considered as being equal to zero the constants m_1, m_2 and m_3 can be determined by fitting relation (A11) to the experimentally determined component flux ratio's as a function of a_i^f. Therefore, a_j^f has to be expressed as a function of a_i^f. This relation can be found from equilibrium sorption experiments in liquid mixtures at different activities.

This has been done for acetic acid/water mixtures using PVC and PAN as the membrane materials. For the water activity range of 0.1 to 1 the following relations for a_a^f as a function of a_w^f can be obtained

PVC: $a_a^f = 1.8880e^{-3} + 7.9140e^{-3}\, a_w^f - 1.9023e^{-3}\, (a_w^f)^2$ (R = 0.998) (A12)

PAN: $a_a^f = 5.3615^{-3} - 3.0145e^{-2}\, a_w^f + 0.15904\, (a_w^f)^2$ (R = 0.998) (A13)

R represents here the correlation coefficient

Fitting relation (A11) using relations (A12) and (A13) results in the curves given in figure A1 (PVC) and figure A2 (PAN), respectively, together with the values for the constants m_1, m_2 and m_3.

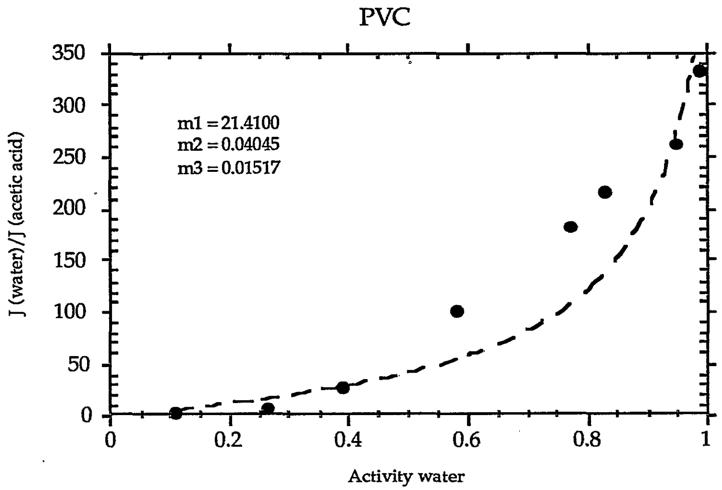

Figure A1 *The water and acetic acid flux ratio as a function of the water activity in the feed mixture for water/acetic acid separation by pervaporation at 80 °C using a PVC membrane; dots (experimental values), line (fitted relation)*

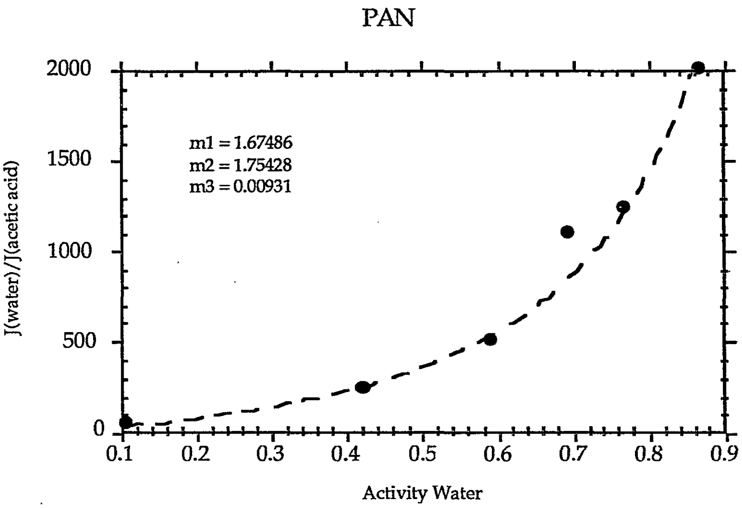

Figure A2 *The water and acetic acid flux ratio as a function of the water activity in the feed mixture for water/acetic acid separation by pervaporation at 80 °C using a PAN membrane; dots (experimental values), line (fitted relation)*

From the curves fitted to the experimentally determined values it can be concluded that the water flux/acetic acid flux ratio through PVC and PAN membranes as a function of the water activity in the feed can be well described by the "exponential 6-parameter model" of Brun.

Reference

A.1 J.P. Brun, C. Larchet, R. Melet and G. Bulvestre, *J. Membr. Sci.*, 23, 257-283 (1985)

APPENDIX

CHEMICAL MODIFICATION OF POLYSULFONE AND POLYETHER-ETHER-KETONE

Synopsis

The influence of sulfonation of polysulfone and polyether-ether-ketone on membrane properties for the dehydration of acetic acid has been studied. As expected the flux of the sulfonated polymer membranes increased with increasing degree of sulfonation, but the selectivity decreased to values which are much too low to be of commercial interest. For sulfonated polyether-ether-ketone the selectivity could be enhanced by chemical crosslinking. As crosslinking agents elemental sulfur and 1,4-phenylenediamine are used successfully. The best pervaporation results were obtained for membranes with 5-10 wt.% 1,4-phenylenediamine; using a feed of 80/20 wt.% acetic acid/water, 8-9 wt.% acetic acid was found in the permeate with a flux of 0.43-0.57 kg/m^{2}h for a membrane thickness of 20 µm. In order to improve the solubility of polyether-ether-ketone, nitration and reaction with highly boiling anilines were studied. Nitration resulted in polymer degradation, but reaction with 3,5-dimethylaniline resulted in a polymer which appeared to be soluble in tetrahydrofuran, chloroform, dimethylformamide and dimethylacetamide. Homogeneous membranes showed 4 wt.% acetic acid in the permeate and a flux of 0.081 kg/m^{2}h using a feed of 80 wt.% acetic acid at 80 °C.

INTRODUCTION

Polysulfone (PSF) and polyether-ether-ketone (PEEK) are highly water selective materials in the dehydration of 80 wt.% acetic acid, despite their hydrophobic character; unfortunately they show moderate fluxes (chapter 2). Introduction of hydrophilic groups onto the polymer back-bone by a chemical reaction will increase the hydrophilicity of the polymer and consequently the membrane flux. Sulfonation is very often used and it can be applied to many polymers [1] including PSF [1-3] and PEEK [4-6].

Since PEEK is a chemically and thermally resistant polymer and only soluble at room temperature in concentrated inorganic acids, like sulfuric acid, chlorosulfonic acid and methanesulfonic acid [7] it is also interesting to study possible chemical modifications of this polymer in order to improve its solubility.

The influence of the degree of sulfonation of PSF and PEEK on flux and selectivity has been studied and is described in this appendix. Also the crosslinking of sulfonated PEEK and other modifications of this polymer like nitration and reaction with anilines were investigated in order to obtain an improved solubility of the polymer.

THEORY

For the sulfonation of PSF two different methods are often used, viz. sulfonation with a sulfur trioxide-triethylphosphate complex [1,2] and sulfonation with chlorosulfonic acid [3]. In our study the latter method is used and the reaction is carried out under mild conditions to avoid polymer degradation.

In figure 1 the chemical structure of PSF is represented and the positions denoted by the letter "b" show the place where the sulfonic acid group will be attached to the polymer. Due to the electron-donating character of the -SO_2- unit the positions "c" and "d" at the neighbouring phenyl group will be deactivated for an electrophilic substitution reaction like sulfonation. Position "a" will not be reactive due to steric hinderance of the -CH_3 group.

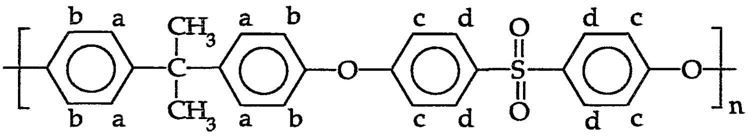

Figure 1 *Chemical structure of polysulfone.*

Marvel et al [6,8,9] have reported that for the sulfonation of PEEK the same methods can be used as for the sulfonation of PSF. However, the disadvantage of the chlorosulfonic acid method is the occurrence of possible crosslinking via the condensation of SO_3H groups [4,6] and the disadvantage of the SO_3/TEP complex method is the extensive degradation and also crosslinking.

A third method of sulfonation is dissolving PEEK in concentrated sulfuric acid. The degree of sulfonation can be controlled by changing the reaction temperature, reaction time and/or sulfuric acid concentration.

This method does not result in degradation nor in crosslinking as long as the acid concentration is kept below 100 % [4]. Sulfonation degrees of 30-100% are possible and take place at the positions "a" and "b" (see figure 2). Positions "c" and "d" are deactivated for the electrophilic reaction by the electron-donating carbonyl group. A disadvantage of this method is the heterogeneity of the sulfonation caused by the relatively slow dissolution of the polymer. Large polymer chains take more time to dissolve which results in shorter reaction times compared to shorter chains; as soon as the polymer chain has been dissolved sulfonation starts.

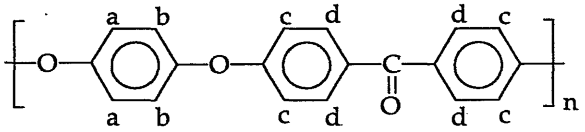

Figure 2 *Chemical structure of polyether-ether-ketone*

Due to the high degree of sulfonation the sorption from an acetic acid/water solution can become so high that the polymer membrane does not show any selectivity. By crosslinking the membrane material the sorption may be reduced, which may result in restoring selectivities. Since, the crosslinking reaction must take place after the membrane has been formed a system must be developed where addition of crosslinking agents to the polymer solution followed by an after-treatment of the ultimately formed membrane results in crosslinking. In literature two possibilities are given to achieve this goal, viz. crosslinking of (sulfonated) PEEK with elemental sulfur [10,11] and crosslinking with phenylenediamine [12].

It is assumed that sulfur consists of polymeric and other reactive radicals at temperatures above 200 °C. These radicals initiate cleavage of the PEEK chains resulting in lower molecular weight chains and crosslinking of the polymer.

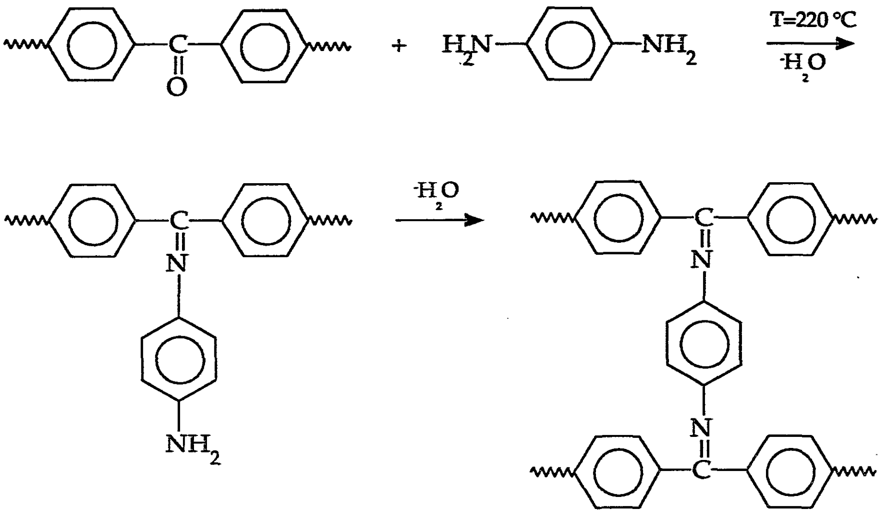

Figure 3 *Crosslink formation of PEEK with 1,4-phenylenediamine*

Phenylenediamine (PDA) contains two functional groups that can react with the carbonyl groups of PEEK under the formation of imine bonds [12,13]. A reaction with two carbonyl groups of different polymer chains results in the formation of crosslinks. The reaction with phenylenediamine is represented in figure 3.

Applying nitration reactions $-NO_2$ units might be introduced at the phenyl groups as well. Several articles dealing with the nitration of aromatic compounds have been published [14-16]. In most nitration reactions pure nitric acid or a combination of nitric acid and concentrated sulfuric acid is used. To avoid water in the reaction mixture a certain amount of oleum or fuming sulfuric acid can be added.

The only functional group of PEEK is the carbonyl group which in principle can react with amines [12,13] (see also figure 3). However, these reactions cannot be carried out in solutions of concentrated acids such as sulfuric acid , methanesulfonic acid or chlorosulfonic acid. Other solvents such as diphenyl sulfone require high temperatures (± 250 °C) and therefore amine compounds must be used with high boiling points in order to carry out chemical modifications in diphenyl sulfone.

EXPERIMENTAL

Materials

Polysulfone (Udel P3500) was obtained from Amoco, polyether-ether-ketone (Victrex PEEK) was obtained from ICI, 3,5-dimethylaniline (98%), diphenyl sulfone (97%) and chlorosulfonic acid (99%) were obtained from Aldrich, elemental sulfur was obtained from Brocades-Stheeman & Pharmacia, nitric acid (65%) and sulfuric acid (95-98%) were obtained from Merck and all other solvents used were of analytical grade and also obtained from Aldrich.

Pervaporation

The pervaporation experiments have been carried out according to the same procedure as described in chapter 2.

Sulfonation of Polysulfone

25 g (56.5 mmol) pre-dried PSF was dissolved in 400 ml distilled 1,2-dichloroethane in a three-necked round-bottomed flask provided with a mechanical stirrer, and a nitrogen in- and outlet. After the polymer was completely dissolved, 1.49 ml (22.48 mmol) chlorosulfonic acid ($ClSO_3H$) in 75 ml distilled 1,2-dichloroethane was added slowly to the polymer solution, using an addition funnel, under vigorous stirring. When all $ClSO_3H$ has been added the reaction mixture should be stirred for at least one hour to be sure the reaction has been completed. The sulfonated polymer precipitates during reaction and can be isolated by filtering and washing with 1,2-dichloroethane. After the sulfonated polymer was dried at 150 °C under vacuum, the polymer was dissolved in dimethylformamide, precipitated in ethanol, filtered, washed and dried at 150 °C for 15 hours under vacuum. This extra purification step has been carried out to remove the low molecular weight polymer and acids produced during the reaction. The amount of $ClSO_3H$ used here, results in a theoretical degree of sulfonation of 0.2; i.e. two SO_3H groups on every 10 repeating units of the polymer.

The degree of sulfonation was calculated from titration experiments as well as from determination of the total sulfur content.

Sulfonation of Polyether-ether-ketone

15 g PEEK pre-dried for at least 4 hours at 150 °C in a vacuum oven is dissolved in 525 ml concentrated sulfuric acid (95-98 %). After 50 hours stirring the polymer solution is precipitated in water cooled with ice. The degree of sulfonation in this case is 0.50; i.e. 5 SO_3H -groups on every 10 repeating units of the polymer.

The degree of sulfonation can be varied by changing the concentration of the sulfuric acid and the residence time in the solution and is calculated from the total sulfur content.

Reaction of PEEK with 3,5-Dimethylaniline

In a 250 ml three-necked round-bottomed flask provided with a mechanical stirrer and a nitrogen in- and outlet, 5 g pre-dried PEEK, 80 g diphenyl sulfone and 10.5 g 3,5-dimethylaniline were brought together. The reaction mixture was heated to a temperature of 270°C in a nitrogen atmosphere. After the polymer had completely dissolved, the solution was cooled down to 250°C. 4 Hours later the reaction mixture was cooled further to room temperature and immersed into acetone to dissolve the phenylene sulfone and unreacted 3,5-dimethylaniline. The polymer was filtered, washed and dried under vacuum at 150 °C. Good solvents for this modified PEEK appeared to be: chloroform, tetrahydrofurane (THF), dimethylformamide (DMF) and dimethylacetamide (DMAc).

RESULTS AND DISCUSSION

Polysulfone

PSF is a hydrophobic, amorphous polymer with high chemical resistance and a moderate selectivity for the dehydration of 80 wt.% acetic acid. Just like PES, PSF is very sensitive for environmental stress-cracking [17]. During evaporation of the casted polymer film stresses can be introduced in the polymeric material. Due to sorption of organic liquids crazes and even cracks might be developed into stressed material. Annealing of these polymers result in better stability.

A higher intrinsic flux can be obtained by increasing the hydrophilicity, which can be achieved by the introduction of sulfonic acid groups.

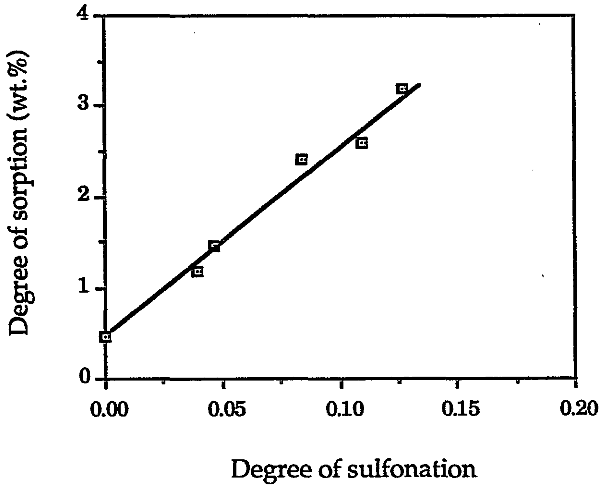

Figure 4 *Water sorption of sulfonated PSF as a function of the degree of sulfonation*

Sulfonated Polysulfone

Polymers with a different degree of sulfonation have been synthesized in order to study the influence on the selectivity and flux.

Figure 4 shows the increase of pure water sorption as a function of the degree of sulfonation. The sorption data represent equilibrium values obtained after 7 days of sorption. A linear increase in sorption with increasing degree of sulfonation can be observed in this figure which has to be attributed to the increase in hydrophilicity.

In figure 5 the selectivity and flux as a function of the degree of sulfonation are given. An expected increase in the flux can be observed with an increasing degree of sulfonation. Unfortunately, the introduction of only a few sulfonic acid groups results in a dramatic decrease of selectivity, which reaches a minimum value of around 50 at a degree of sulfonation of 0.08. Further increase of sulfonation does not influence the selectivity anymore. A degree of sulfonation higher than 0.25 results in a polymer that dissolves in the acetic acid/water mixture at 80 °C.

Summarizing it can be concluded that an increase in flux can be achieved by introducing hydrophilic groups, but this results in a dramatic decrease in selectivity.

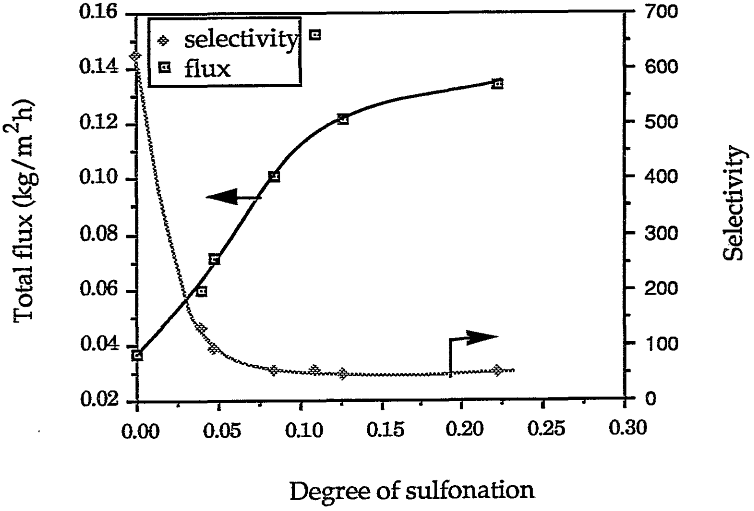

Figure 5 *Selectivity and flux of sulfonated PSF as a function of the degree of sulfonation*

Polyether-ether-ketone

PEEK is a highly chemically resistant polymer and as a result at room temperature only soluble in very strong concentrated acids, like e.g. concentrated sulfonic acid, chlorosulfonic acid and methane sulfonic acid. These solvents are not particularly users friendly and besides, the first two solvents result in sulfonation of the polymer.

In order to obtain a polymer which is soluble in the more common solvents such as THF, DMF and DMAc several ways of chemical modification of PEEK have been studied.

Sulfonated Polyether-ether-ketone

It appeared that sulfonated PEEK becomes soluble in solvents like DMF, DMAc and dimethylsulfoxide (DMSO) as the degree of sulfonation is about 0.48, which means 48 sulfonic acid groups per 100 repeating units of the polymer main chain. A degree of sulfonation higher than 0.55 results in polymers that dissolve in acetic acid/water mixtures at 80 °C. In table 1 the selectivity and flux of several sulfonated PEEK membranes are represented

Table 1 *Permeate composition and flux of sulfonated PEEK membranes for the dehydration of 80 wt.% acetic acid at 80 °C*

Polymer	degree of sulfonation	casting solvent	feed (wt.% acid)	permeate (wt.% acid)	flux* (kg/m²h)
PEEK 65	0.55	DMF	dissolved during pervaporation		
PEEK 50	0.50	DMF	81.10	32.70	3.36
PEEK 50	0.50	DMF	81.50	30.90	5.86
PEEK 40	0.48	DMF	79.40	30.10	5.16
PEEK 40	0.48	DMSO	80.80	25.90	3.11
PEEK 40	0.48	DMSO	80.40	24.50	2.88
PEEK 30		DMSO	80.10	30.60	3.54
PEEK 30		DMAc	81.00	35.70	5.07

* flux is normalized to a membrane thickness of 20 μm

using a feed of 80 wt.% acetic acid at 80 °C.

The numbers behind PEEK in the first column of table 1 represent the hours the polymer remained dissolved in concentrated sulfuric acid. From this table it can be concluded that there is no real trend between degree of sulfonation and selectivity and flux. Since the difference in degree of sulfonation is very small this is not unexpected. Besides, the sulfonic acid groups will not be uniformly distributed over the polymer chain. This is caused by the relatively long time the polymer needs to dissolve completely; the parts that dissolve almost immediately will contain a higher amount of sulfonic acid groups compared to the parts that dissolve 5-7 hours later.

Using DMSO as a solvent, which appears to be the best solvent for sulfonated PEEK, a somewhat higher selectivity was obtained combined with a lower flux. Generally, it can be concluded that the selectivities are too low for the dehydration of acetic acid and the fluxes are extremely high, due to the enormous degree of sorption (see table 7, chapter 2).

Crosslinking of Sulfonated Polyether-ether-ketone

Crosslinking of sulfonated PEEK restricts the degree of sorption which may result in higher selectivities and lower fluxes. For sulfonated PEEK three different crosslinking possibilities have been studied and will be discussed.

Elemental Sulfur

Crosslinked sulfonated PEEK membranes were obtained by addition of 0.5-2 wt.% elemental sulfur to the polymer solution. After the membrane has been formed by solution casting, and evaporation in a nitrogen atmosphere and drying in a vacuum oven at 80 °C, a heat treatment was applied of 3-4 hours at 250 °C in a nitrogen atmosphere. Some data of these crosslinked sulfonated PEEK membranes are represented in table 2.

Although, the selectivity has become 2-3 times higher the separation properties are not spectacularly improved compared to the uncrosslinked membranes. The selectivity is still too low and a decrease of flux with increasing crosslinking density was observed.

Table 2 *Permeate composition and flux of sulfonated PEEK membranes crosslinked with elemental sulfur for the dehydration of 80 wt.% acetic acid at 80 °C*

Polymer	Sulfur (wt.%)	feed (wt.% acid)	permeate (wt.% acid)	flux* (kg/m^2h)
PEEK(SO_3)	0.5	79.10	17.9	1.82
PEEK(SO_3)	0.5	79.90	12.30	1.12
PEEK(SO_3)	1.0	76.60	16.40	0.93
PEEK(SO_3)	2.0	79.70	16.20	0.46

* flux is normalized to a membrane thickness of 20 µm

1,4-Phenylenediamine

Crosslinked membranes with 1,4 phenylenediamine (PDA) are prepared by the addition of a certain amount of PDA to the casting solution. Evaporation of the solvent from the casted film in a nitrogen atmosphere and drying the membrane under vacuum at 150 °C are followed by a heat treatment at 230 °C. The influence of crosslinking with different amounts of PDA on selectivity and flux is represented in tables 3 and 4.

Table 3 *Selectivity and flux of PEEK(SO_3)$_{0.5}$ crosslinked with p-phenylenediamine for the dehydration of 80 wt.% acetic acid at 80 °C*

PDA (wt.%)	heat treatment	feed (wt.% acid)	permeate (wt.% acid)	selectivity	flux* (kg/m^{2}h)
0	none	80.40	24.50	12	2.88
3	none	80.60	19.70	17	2.04
5	4 hrs. (230°C)	81.40	9.40	51	0.57
10	none	80.70	9.90	39.6	0.47
10	4 hrs. (230°C)	79.40	8.00	44.3	0.43
20	none	79.50	9.30	38	0.53

* flux is normalized to a membrane thickness of 20 μm

From table 3 it can be concluded that addition of PDA to the polymer solution results in membranes with higher selectivities. Table 3 also shows that 5-10 wt.% PDA gives the best results. Addition of more than 10 wt.% does not result in a higher crosslinking density. Furthermore, it appeared that a heat treatment at 150 °C (24 hrs), applied to all membranes, results in almost the same separation properties as a heat treatment at 230 °C (4 hrs). This means that this crosslink formation is not only temperature dependent, but also time dependent. A heat treatment at 230-250 °C for a longer period of time might result in even higher selectivities. The membranes crosslinked with PDA show higher selectivities compared to the membranes crosslinked with elemental sulfur.

Table 4 *Selectivity and flux of PEEK(SO_3)$_{0.5}$ crosslinked with p-phenylenediamine for the dehydration of 98 wt.% acetic acid at 80 °C*

PDA (wt.%)	heat treatment	feed (wt.% acid)	permeate (wt.% acid)	selectivity	flux (kg/m^{2}h)
0	none	98.10	89.40	6.1	0.932
3	none	97.00	64.30	18.0	0.098
5	4 hrs. (230°C)	98.00	55.30	39.6	0.048
10	none	98.10	57.40	38.3	0.057
10	4 hrs. (230°C)	97.60	46.80	46.2	0.039

Table 4 represents the separation properties of PDA crosslinked sulfonated PEEK membranes for the dehydration of 98 wt.% acetic acid. Compared to the uncrosslinked membrane the selectivity has been improved, but about 50 wt.% acetic acid in the permeate is far too high.

The improvement of selectivity by crosslinking is clearly shown in figure 6, where the permeate composition is plotted as a function of the acetic acid/water feed composition together with the vapour-liquid equilibrium curve.

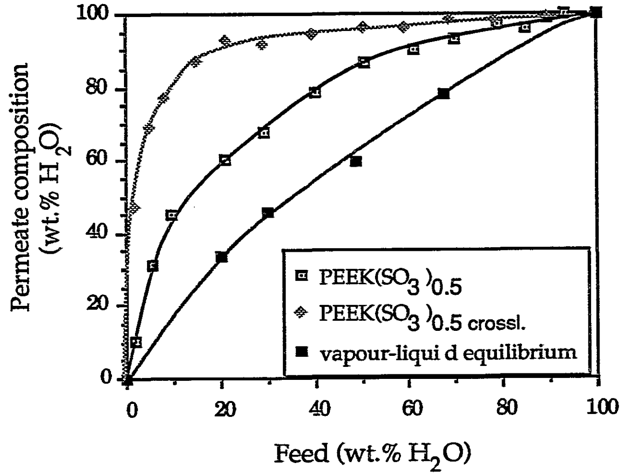

Figure 6 *Permeate composition of crosslinked and uncrosslinked sulfonated PEEK membranes as a function of the feed composition for the dehydration of acetic acid by pervaporation at 80 °C; the vapor-liquid equilibrium of acetic acid/water mixtures at 80 °C is also given*

From figure 6 it can be seen that at low acetic acid concentrations in the feed the acetic acid rejection of both membranes is much higher than the rejection of commercially available reverse osmosis membranes (table 3, chapter 1). In figure 7 fluxes of the uncrosslinked as well as of the crosslinked sulfonated PEEK membranes are given.

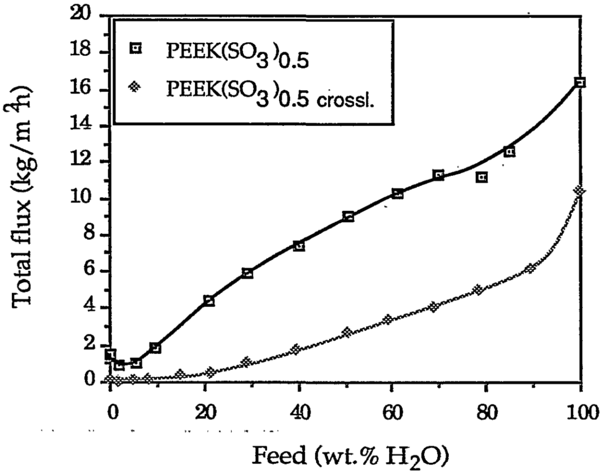

Figure 7 *Total flux of crosslinked and uncrosslinked sulfonated PEEK membranes as a function of the feed composition for the dehydration of acetic acid at 80 °C*

Due to the extremely high permeability of these membranes (figure 7) sulfonated PEEK membranes can be very well used for the after treatment of the permeate in the dehydration process. Table 5 represents the rejection and flux of sulfonated PEEK membranes for a membrane thickness of 10 µm.

Table 5 *Rejection and flux of sulfonated PEEK membranes as a function of the feed composition in pervaporation*

Membrane	feed (wt.% acid)	rejection (%)	flux* (kg/m²h)	process**
$PEEK(SO_3)_{0.5}$	6.90	96.4	29	PV
$PEEK(SO_3)_{0.5}$	10.70	91.8	25	PV
$PEEK(SO_3)_{0.5}$	21.00	85.7	45	PV
$PEEK(SO_3)_{0.5\ \text{crossl.}}$	10.50	91.6	12	PV
$PEEK(SO_3)_{0.5\ \text{crossl.}}$	21.30.	93.2	10	PV
PEC 1000	10.0	84.0	6	RO

* flux normalized to a membrane thickness of 10 µm

** PV: pervaporation; RO: reverse osmosis (operating conditions: 56 kg/cm², 25 °C)

CONCLUSIONS

Sulfonation of both PSF and PEEK has been successfully applied and resulted in high flux membranes. However, the selectivity decreased dramatically, so that it can be concluded that the separation properties were not satisfactorily improved.

Crosslinking of the sulfonated PEEK membranes with both elemental sulfur and phenylenediamine did result in higher selectivities. The best results were obtained with 5-10 wt.% phenylenediamine as a crosslinking agent; 8-9 wt.% acetic acid in the permeate and a flux of 0.43-0.57 kg/m^{2}h has been obtained using a feed of 80 wt.% acetic acid at 80°C.

At low acetic acid concentrations in the feed the uncrosslinked as well as the crosslinked sulfonated PEEK membranes appeared to be water selective to such an extent that the rejection of acetic acid is higher than values known for commercially available reverse osmosis membranes. Besides, the fluxes of these sulfonated membranes are high enough to compete with reverse osmosis. These membranes can thus be applied very well for the treatment of the permeate streams in dehydration processes, which contain 5-10 wt.% acetic acid.

Furthermore, it can be concluded that nitration of PEEK with mixtures of sulfuric acid and nitric acid results in polymer degradation as the nitric acid concentration becomes too high. A degree of nitration of 1.5 appeared to be insufficient to obtain a polymer which is soluble in solvents like e.g. dimethylformamide, tetrahydrofuran, dimethylacetamide.

Reaction of PEEK with 3,5-dimethylaniline on the other hand did result in a polymer which is soluble in the more common solvents as just mentioned. The membrane separation properties of this modified PEEK lies in between the properties of crosslinked sulfonated PEEK and unmodified PEEK; 4 wt.% acetic acid in the permeate and a flux of 0.081 kg/m^{2}h has been obtained using a feed of 80 wt.% acetic acid at 80 °C.

Overall, it can be concluded that chemical modification of stable polymeric membranes (PEEK and PSF) is not a good approach to improve membrane separtion performance.

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SUMMARY

Acetic acid/water mixtures are found in the chemical industry in the production of acetic acid, vinyl acetate, acetic anhydride, terephthalic acid, etc. For the separation of these mixtures normally techniques like fractionation distillation, azeotropic distillation and liquid-liquid extraction are used. These separation techniques consume quite amounts of energy and therefore there is a demand for new and cheaper techniques. One of these cheaper alternatives might be pervaporation, a membrane separation process which is extremely suitable for the dehydration of organic solvents. The membranes used in pervaporation have to be sufficiently selective and permeable to be of economical interest. Applied to the dehydration of acetic acid at elevated temperatures the chemical and thermal resistance of the membrane material is also very important. At a feed composition of 80/20 wt.% acetic acid/water at 80 °C the aimwas to develop membranes with a selectivity of at least 200 and a flux of 0.5 kg/m^{2}h. At a feed composition of 98/2 acetic acid/water the target selectivity remains to 200 with a flux of at least 0.2 kg/m^{2}h. In this study suitable membrane materials have been selected (chapter 2) and two different types of membranes have been developed, viz. a polysulfone hollow fiber membrane (chapter 3) and a flat sheet polyvinylchloride/polyacrylonitrile composite membrane (chapter 5).

Chemical stability experiments and pervaporation experiments were carried out in order to select chemically resistant membrane materials with a high selectivity towards water. Polysulfone (PSF), polyethersulfone (PES), polyacrylonitrile (PAN), polyvinylchloride (PVC) and polyether-ether-ketone (PEEK) are satisfactory in resistance and show selectivities higher than 250 using a feed solution of 80/20 wt.% acetic acid/water at 80 °C. From sorption experiments it could be concluded that the selectivity of these materials is mainly determined by the difference in diffusion rate between acetic acid and water rather than by a difference in preferential sorption; the sorption selectivity is close to unity and for PVC and PSF even in favour towards acetic acid.

From PSF integrally skinned hollow fiber membranes have been spun by a phase inversion technique resulting in a defect-free toplayer. For the spinning process applied a specially designed spinneret was developed which allows spinning without an air gap. This spinneret makes it possible to use two different nonsolvents subsequently. During the contact time with the first nonsolvent the polymer concentration at the outer

ZUSAMMENFASSUNG

Bei der industriellen Herstellung von Essigsäure, Vinylacetat, Essigsäureanhydrid und Terephtalsäure fallen häufig Essigsäure/Wasser Produktströme an, die üblicherweise durch fraktionierte Destillation bzw. Schleppmitteldestillation oder durch Extraktionsverfahren getrennt werden. Diese Trennverfahren zeichnen sich durch einen sehr hohen Energieverbrauch aus. Pervaporation, ein Membrantrennprozess, der sehr gut geeignet ist für die Entwässerung von organischen Lösemitteln, kann eventuell eine energiegünstige Alternative zu den herkömmlichen Trennverfahren darstellen.

Die hierfür ausgewählten Membranen müssen, um ökonomisch interessant zu sein, genügend selektiv und permeabel sein. Im Falle der Trennung von Essigsäure/Wasser Gemischen, müssen diese Membranen auch noch chemisch und thermisch stabil sein, da die Trennung bei 80°C und einer Feedzusammensetzung von 80% Essigsäure und 20% Wasser ausgeführt werden soll. Die Membran muß eine Mindestselektivität von 200 und einen Fluß von 0.5 kg/m^{2}h aufweisen, um mit anderen Trennverfahren konkurieren zu können. Für eine Gemischzusammensetzung von 98% Essigsäure und 2% Wasser muß die Membran weiterhin eine Selektivität von 200 besitzen; eine Flußreduktion von 0.5 nach 0.2 kg/m^{2}h ist jedoch akzeptabel.

In der vorliegenden Arbeit werden polymere Materialien selektiert, die die benötigten Eigenschaften bzgl. Selektivität, Fluß, chemischer und thermischer Stabilität besitzen (Kapitel 2). Aus den genannten Materialien werden zwei verschiedene Membranen hergestellt, eine Polysulfonhohlfasermembran (Kapitel 3) und eine Kompositflachmembran aus Polyvinylchlorid, als selektive Schicht, aufgebracht auf einer Polyacrylnitril Trägermembran.

Neben den üblichen Pervaporationsexperimenten wird die chemische Stabilität in Langzeitversuchen intensiv studiert. Polysulfon, Polyethersulfon, Polyacrylnitril, Polyvinylchlorid und Polyetheretherketon zeigen eine ausreichende chemische Stabilität und genügend hohe Selectivitäten. Aus den Resultaten von Sorptions- und Permeationsexperimenten kann geschlossen werden, daß die Selectivität dieser Materialien hauptsächlich durch unterschiedliche Diffusionskonstanten der beiden Komponenten bestimmt wird. Der Sorptionstrennfaktor liegt in der Regel bei ungefähr 1 oder wird, wie im Falle von PVC und PSF sogar kleiner als eins.

Aus PSF wurden integralgesponnene Hohlfasermembranen mit defektfreien, gasdichten Schichten gesponnen. Für den sogenannten Zweibadspinnprozess wurde ein neuer Spinnkopf entworfen, der das Spinnen der Hohlfaser ohne Kontakt mit der Umgebungsluft ermöglicht. Hierbei können zwei verschiedene, direkt aufeinanderfolgende Fällmittel benutzt werden. Während der Kontaktzeit mit dem ersten, schwachen Fällmittel wird die Polymerkonzentration an der Außenseite der Hohlfaser erhöht. Beim Kontakt mit dem zweiten, starken Fällmittel, dem eigentlichen Koagulationsbad, tritt Phasentrennung und Verfestigung zur letztendlichen Membran auf. Selective Außenschichten von 1µm Dicke, getragen von einer porösen Stützschicht, konnten hergestellt werden. Elektronenmikroskopie und Pervaporationsexperimente wurden angewandt, um den Effekt verschiedener Herstellungsparameter auf die Membranstruktur und Permeationseigenschaften zu charakterisieren. Hohe Flüsse als Folge von verringertem Stofftransportwiderstand in der Stützmembran konnten durch das Zumischen von Glycerol zur Polymerlösung, durch die Erniedrigung der Polymerkonzentration und durch Zufügen von Lösungsmittel in das innere Fällungsbad erreicht werden. Weiterhin wurde der Einfluß der Art des Lösungsmittels in der Polymerlösung und die Art des ersten Fällbades studiert. Die besten Hohlfasern zeigen einen Fluß von 0.46-0.51 kg/m^{2}h and Selektivitäten von 64-72.

Die relativ niedrigen Selektivitäten der PSF Hohlfasermembranen werden in Kapitel 4 untersucht. Experimente mit verschieden dicken homogenen Membranen aus PSF, PVC und PAN zeigen, daß die Selektivitäten dieser Membranen stark von der Membrandicke abhängen. Unterhalb einer kritischen Dicke von ca. 15 µm nimmt die Pervaporationsselektivität drastisch ab, die Selektivität in Gastrennungsexperimenten mit CO2/CH4 Gasgemischen bleibt jedoch konstant. Dieses Phenomen kann nicht durch unterschiedliche Membranmorphologien, Sorptionswiderstand oder thermodynamischer Transportkopplung erklärt werden. Es wird aufgezeigt, daß dieser Selektivitätsverlust bei dünnen Membranen im Zusammenhang steht mit Defekten, die während des eigentlichen Pervaporationsexperiments entstehen. Diese Defekte, sogenannte Crazes, die Vorläufer von Mikrorissen sind, entstehen aufgrund eines erniedrigten kritischen Dehnungsniveaus durch den Quelleffekt der absorbierten Penetrantmoleküle. Stressgradienten in der Polymermatrix entstehen durch das Konzentrationsprofil der Penetrantmoleküle in der Membran.

Außerdem wurde eine Kompositmembran, die aus einer selectiven

PVC-Schicht auf einer PAN-Trägermembran besteht, entwickelt. Mit dieser Membran wurde der Einfluß der Oberflächenporosität der Trägermembran auf Gesamtfluß und Selektivität bestimmt. Hierbei stellte sich heraus, daß mit abnehmender Oberflächenporosität die Selektivität zunimmt, insbesondere bei Feedmischungen mit hohem Essigsäuregehalt. Aus diesen Resultaten kann gefolgert werden, daß die Trägermembran wesentlich zum Gesamtverhalten der Membran beiträgt. Obwohl die Oberflächenporosität sehr gering ist, konnten hohe Gesamtflüsse erreicht werden. Bei einer Feedzusammensetzung von 80/20 gew.% Essigsäure /Wasser und 80°C Feedtemperatur bewegten sich die Selektivitäten im Bereich von 182-274 und die Flüsse von 0.56 bis 0.74 kg/m^{2}h. Bei einer Feedzusammensetzung von 98/2 gew% Essigsäure/Wasser blieb die Selectivität in der gleichen Größenordnung (206-261), während der Fluß auf Werte von 0.14-0.15 kg/m^{2}h abfiel.

Der Einfluß der chemischen Modification von PSF und PEEK auf Trenneigenschaften and die Verbesserung des Löslichkeitsverhalten von PEEK werden im Appendix dieser Arbeit beschrieben. Die Sulfonierung der beiden Polymere hatte eine drastische Erhöhung und einen Selectivitätsverlust zur Folge. Jedoch konnte die Selectivität von sulfoniertem PEEK durch nachträgliches, chemisches Vernetzen mit elementarem Schefel oder 1,4-Phenylendiamin wiederum verbessert werden. Die besten Resultate wurden mit 5-10 gew% 1,4 Phenylendiamin errreicht; bei einer Feedzusammensetzung von 80/20 gew% Essigsäure/Wasser wurden mit einer 20 µm dicken Membran eine Selektivität von 40-46 und Flüsse von 0.43-0.57 kg/m^{2}h erreicht.

Zur weiteren Verbesserung des Löslichkeitsverhaltens von PEEK wurden Nitrierungsexperimente und Reaktionen mit hochsiedenden Anilinen ausgeführt. Allerdings degradierte das Polymer während der Nitrierungsreaktion. Die Reaktion mit 3,5-Dimethylaniline führte zu einem Polymer, das löslich ist in Tetrahydrofuran, Chloroform, Dimethylformamid und Dimethylacetamid. 20 µm dicke Membranen aus diesem Polymer zeigten Selektivitäten von 89 und einen Fluß von 0.081 kg/m^{2}h bei den üblichen Prozessparametern.

SAMENVATTING

In de chemische industrie komt men azijnzuur/water mengsels tegen bij de productie van o.a. azijnzuur, vinylacetaat, azijnzuuranhydride en tereftaal-zuur. Scheidingsprocessen die normaliter voor de scheiding van deze mengsels gebruikt worden zijn: gefractioneerde destillatie, azeotropische destillatie en vloeistof-vloeistof extractie. Omdat deze technieken nogal veel energie verbruiken zijn nieuwe en vooral goedkopere scheidingstechnieken gewenst.
Een goedkoper aternatief zou wellicht pervaporatie kunnen zijn. Pervaporatie is een membraanscheidingproces dat uitermate geschikt is voor het ontwateren van organische oplosmiddelen. Om te kunnen concurreren met de huidige scheidingstechnieken moeten de membranen die gebruikt worden voor pervaporatie voldoende selectief en voldoende permeabel zijn. Tevens moet het membraanmateriaal resistent zijn tegen degradatie door het te scheiden mengsel, in dit geval geconcentreerde azijnzuuroplossingen bij 80-90 °C. Bij gebruik van een voedingsmengsel van 80/20 gew.% azijnzuur/water bij 80 °C is een selectiviteit gewenst van tenminste 200 en een flux van tenminste 0.5 kg/m^{2}h; bij gebruik van een voedingsmengsel van 98/2 gew.% azijnzuur/water bij 80 °C is de gewenste selectiviteit nog steeds 200 en de gewenste flux tenminste 0.2 kg/m^{2}h. Gedurende deze studie is gezocht naar geschikte membraanmaterialen (hoofdstuk 2) en zijn twee verschillende type membranen ontwikkeld, teweten een polysulfon holle vezel membraan (hoofdstuk 3) en een polyvinylchloride/polyacrylonitril composiet membraan (hoofdstuk 5).

Experimenten om de chemische stabiliteit en de pervaporatieselectiviteit te bepalen zijn uitgevoerd. De polymeren polysulfon (PSF), polyethersulfon (PES), polyacrylonitril (PAN), polyvinylchloride (PVC) en polyether-ether-keton (PEEK) bleken voldoende resistent in geconcentreerd azijnzuur en vertoonden alle een selectiviteit hoger dan 250 bij gebruik van een 80/20 gew.% azijnzuur/water voedingsmengsel bij 80 °C. Uit sorptiemetingen kan worden geconcludeerd dat de pervaporatieselectiviteit van deze materialen bepaald wordt door het verschil in diffusiesnelheid van water en azijnzuur en niet door een verschil in preferentiële sorptie; de sorptieselectiviteit ligt dicht bij 1, en PVC en PSF sorberen zelfs preferentiëel azijnzuur.

Van PSF zijn integraal geskinde holle vezel membranen gesponnen met een defect-vrije toplaag. Voor het toegepaste spinproces, het zogenaamde "twee-bads spinproces", werd een speciale spinkop ontwikkeld

die het mogelijk maakt te spinnen zonder luchttraject. De spinkop bevat een extra cilindrische opening waardoor de mogelijkheid onstaat twee verschillende niet-oplosmiddelen, na elkaar in contact te brengen met de "vezel-in-wording". Gedurende het contact met het eerste niet-oplosmiddel ontstaat een verhoogde polymeerconcentratie aan de buitenkant van de vezel, waarna een tweede niet-oplosmiddel, het coagulatiebad, voor verdere fase scheiding en uitharden van de uiteindelijke vezel zorgt. Toplagen van ± 1 μm ondersteunt door een poreuze sublaag konden worden verkregen. Spinparameters die mogelijk van invloed zijn op de membraanstructuur en daardoor ook op de scheidingseigenschappen zijn onderzocht m.b.v. de scanning electron microscoop en d.m.v. pervaporatie-experimenten, waarbij een voeding van 80/20 gew.% azijnzuur/water bij 70 °C is gebruikt. Als gevolg van een verlaagde weerstand in de steunlaag werden hogere fluxen verkregen door het toevoegen van glycerol aan de polymeeroplossing, door het verlagen van de polymeerconcentratie in de polymeeroplossing en door het toevoegen van oplosmiddel aan de lumenvloeistof. Andere onderzochte parameters zijn: het type oplosmiddel in de polymeeroplossing en het type niet-oplosmiddel dat gebruikt wordt als eerste niet-oplosmiddel om de polymeerconcentratie aan de buitenkant van de vezel te verhogen. Vezels met een selectiviteit van 64-72 en een flux van 0.46-0.51 kg/m^{2}h zijn verkregen.

De relatief lage selectiviteit van deze PSF vezels is bestudeerd in hoofdstuk 4. Uit een studie waarbij de pervaporatieselectiviteit van PSF, PVC en PAN membranen werd onderzocht als een functie van de membraandikte kon worden geconcludeerd dat de selectiviteit dikte afhankelijk wordt beneden een bepaalde limietwaarde; deze ligt rond de 15 μm. Voor gasscheiding blijkt de selectiviteit van PSF membranen onafhankelijk te zijn van de membraandikte. Dit verschijnsel kan niet worden verklaard door een verschil in membraanmorfologie, sorptieweerstand, thermodynamische interactie of "koppeling". De verklaring voor de selectiviteitsafname bij dunnere membrane moet gezocht worden in het ontstaan van defecten tijdens de pervaporatiemeting. Deze defecten, crazes (en cracks) kunnen ontstaan door een verlaagde waarde van de kritische rek, als gevolg van azijnzuur/water sorptie en door spanningen tussen de polymeerketens, als gevolg van een concentratiegradiënt over het membraan.

Naast een integraal geskind membraan werd ook een composiet-membraan ontwikkeld, bestaande uit een PVC toplaag en een PAN steunlaag. De invloed van de oppervlakte porositeit van de steunlaag op de selectiviteit en flux van de composietmembraan is onderzocht. De experimenten laten zien dat de selectiviteit toeneemt als de porositeit afneemt; dit treedt vooral op bij hoge azijnzuurconcentraties in de voeding. Daaruit kan worden geconcludeerd dat de steunlaag bijdraagt aan de selectiviteit van het composietmembraan. Ondanks de lage oppervlakteporositeit kunnen toch hoge fluxen bereikt worden. Bij gebruik van een 80/20 gew.% azijnzuur/water voedingsmengsel bij 80 °C werden selectiviteiten van 182-274 en fluxen van 0.56-0.74 kg/m^{2}h verkregen. Een voeding van 98/2 gew.% azijnzuur/water bij 80 °C resulteerde in selectiviteiten van 206-261 en fluxen van 0.14-0.15 kg/m^{2}h.

De invloed van chemische modificatie van PSF en PEEK op de scheidings-eigenschappen en de oplosbaarheid van PEEK staan beschreven in de appendix. Sulfonering van beide polymeren resulteerde in een sterke toename van de flux, gepaard met een sterke afname in selectiviteit. De selectiviteit van gesulfoneerd PEEK kan weer verhoogd worden d.m.v. het aanbrengen van chemische "crosslinks", hetzij met behulp van zwavel, hetzij met behulp van 1,4-fenyleendiamine. Het beste resultaat wordt verkregen bij gebruik van 5-10 gew.% 1,4-fenyleendiamine; een voeding van 80/20 gew.% azijnzuur/water bij 80 °C resulteert in een selectiviteit van 40-46 en een flux van 0.43-0.57 kg/m^{2}h voor pervaporatie bij gebruik van een 20 µm dik membraan. Om de oplosbaarheid van PEEK te verbeteren is de nitrering van PEEK en reacties van PEEK met anilines onderzocht. De nitrering resulteerde in degradatie van het polymeer, maar de reactie met 3,5-dimethylaniline resulteerde in een polymeer dat oplosbaar is in tetrahydrofuraan, chloroform, dimethylformamide en dimethylacetamide. Membranen van dit polymeer met een dikte van 20 µm gaf een selectiviteit van 89 en een flux van 0.081 kg/m^{2}h te zien bij een voeding van 80/20 gew.% azijnzuur/water bij 80 °C.

LEVENSLOOP

Geert-Henk Koops werd geboren op 23 december 1964 te Ommen. Hij volgde de lagere school in Dalfsen en het atheneum aan "het Meander College" te Zwolle, alwaar hij in 1983 het diploma behaalde.
In datzelfde jaar begon hij de studie Chemische Technologie aan de Universiteit Twente waar hij op 25 maart 1988 afstudeerde bij de onderzoekgroep Membraantechnologie onder leiding van prof. dr. C.A. Smolders.

Per 1 april 1988 trad hij in dienst als assistent in opleiding (AIO) bij dezelfde onderzoekgroep, alwaar het in dit proefschrift beschreven onderzoek werd uitgevoerd.

Per 10 augustus 1992 zal hij als Research Fellow zijn carrière vervolgen in Japan bij het Industrial Products Research Institute te Tsukuba in de groep van Dr. S. Yamada.