PERVAPORATION

membranes and models for the dehydration of ethanol

Polyvinylalcohol
mEmbrane
peRmeability
selectiVity
ethAnol
Polyacrylonitrile
sOlution
disseRtation
vAcuum
waTer
dIffusion
hOmogeneous
thickNess

Jos Spitzen

12

PERVAPORATION

membranes and models
for the dehydration of ethanol

PROEFSCHRIFT

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Assistent promotor: dr. ing. M.H.V. Mulder

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Voorwoord

Een proefschrift wordt in het algemeen aan de naam van de auteur gekoppeld. De auteur brengt een proefschrift echter niet in een 'vacuum' tot stand, maar in een omgeving van collega's.

Op de eerste plaats is dit een omgeving die de auteur stimuleert, corrigeert en met hem discussieert. In dit kader wil ik met name noemen Kees Smolders en Marcel Mulder, die ik hierbij dank voor de plezierige begeleiding in de afgelopen 4 jaren.

Bovendien is dit een omgeving die hem ondersteuning biedt op velerlei praktisch gebied. Het met name noemen van alle personen die mij op dergelijke wijze hebben geholpen, zou resulteren in een te lange opsomming, met het gevaar dat ik namen zou vergeten. Ik bedank dan ook een ieder die in de afgelopen 4 jaar, op welke wijze dan ook, heeft bijgedragen aan het onderzoek dat in dit proefschrift is beschreven.

En 'last but not least', in deze omgeving moeten het werkklimaat en de sfeer goed zijn. In de werkgroep Membraanfiltratie kwam dit met name tot uiting in de koffie- en lunchpauzes, de voetbal- en volleybalcompetitie en de jaarlijkse fietstochten en andere uitstapjes.

Wanneer ik terug kijk op deze 'promotie-jaren' dan doe ik dat met veel vreugde, ... en met een beetje weemoed.

Contents

Chapter 1

Introduction.

1.1 The role of separation processes in the chemical industry

In the chemical industry the ultimate goal of all efforts can be formulated as 'the production of certain desired chemicals, that are demanded by potential and existing markets, on the basis of a number of basic materials or intermediate products'. Although the basic process to obtain the desired products from some other chemicals is of course a chemical reaction, the overall production process can be divided into three main steps:

- *the pre-treatment of the basic materials:* before the basic materials can be used optimally in the chemical reactions, usually they need purification, control of physical state (solid/liquid/gas), pressure, concentration, temperature.
- *the chemical reaction(s):* taking place at the optimal reaction conditions.
- *the post-treatment of the reaction products:* after the essential chemical reactions have taken place (or after a certain conversion is obtained) the desired reaction products have to be separated from the unreacted materials and from the by-products. The unreacted materials usually can be recycled to the reactor, and the desired products generally have to be separated from each other, purified, and set to the desired physical state (solid/liquid/gas), pressure, concentration, temperature, and put into the desired product dimensions.

The sequence of these processes is given schematically in figure 1.1 [1.1] (for completeness storage and transport of materials and products should be added).

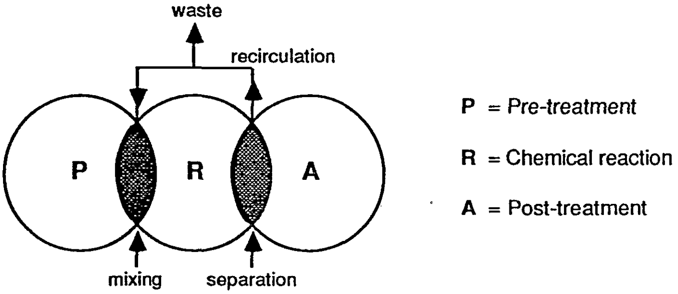


Figure 1.1: Schematic representation of a production process in the chemical industry.

The shaded areas represent the intermediate processes between the treatments P and R, respectively R and A, and are usually related to mixing or separation of materials. The recirculation of the unreacted materials is taking place between these two shaded areas.

From this scheme it can be concluded that the actual chemical reactions, although essential, represent only a small part in production processes in the chemical industry. Because purification can also be considered as a separation process, it is clear that *separation processes* are very important in the total production processes in the chemical industry.

Separation processes generally are based on differences in physical and/or chemical nature of the components to be separated, and can be divided in *phase separation* techniques and *component separation* techniques.

In the case of a phase separation process the feed consists of two (or more) separate phases. These processes generally make use of differences in physical properties of the components in the two phases, such as differences in mass or density (filtration, centrifugation, flotation, dust collection, particle separation, liquid-liquid phase separation), or in particle size (sieving, filtration, pressing).

In component separation processes the feed is mixed at a molecular level, and separation into the separate components is more difficult compared to phase separation. In these cases generally differences in chemical properties are used, such as differences in vapour pressure (distillation, stripping, evaporation, drying), chemical nature (leaching, complexation, chromatography), affinity (adsorption, absorption, extraction, perstraction), freezing point (crystallization), or charge (ion exchange).

Although the existing industrial separation techniques are still being optimized, a lot of research is focussed at the development of new separation techniques and to the commercialization of promising techniques, aiming at a decrease of energy consumption and of investment costs.

1.2 Membrane filtration

A new separation technique that has only recently been developed for technical applications and is under commercialization, is *membrane filtration.* Actually, membrane filtration is the name of a class of separation processes, in which the separation of a mixture of components is obtained by means of a membrane. A membrane can be defined as a selective barrier between two phases. A schematic representation of a membrane is given in figure 1.2. Separation is based on differences in transport rates of the components through the membrane matrix. Membranes can be prepared from organic and inorganic materials, and can in principle consist of a solid, a liquid or a gaseous phase. Until now most membranes are solid based, liquid membranes are under development, whereas no examples of gaseous membranes do exist yet.

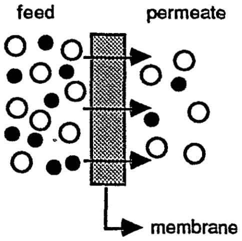


Figure 1.2: Schematic representation of a semi-permeable membrane, separating the feed from the permeate.

Although classical filtration is a rather common and old separation technique, the use of membranes provides some interesting new features and possibilities. Classical filtration makes use of the differences in size of the separating components, but only at a super-macromolecular level, and thus can be considered as a phase separation technique. It is mainly used to separate solids from liquids or gases. The separation characteristics of the process are only determined by the size of the pores or the mesh of the filter medium.

In contrast to classical filtration, most membrane filtration processes can be considered as a component separation technique. Mixtures of components that are mixed at a molecular level can be separated. Therefore membrane separation processes can compete with existing component separation techniques.

The main advantages of membrane separation processes, compared to existing techniques, are:

1. membrane filtration is a relatively simple technique.
2. membrane processes can be operated continuously.
3. membrane processes can easily be combined with other separation techniques (flexibility).
4. most membrane processes can be operated at low or moderate temperatures (important for biological applications).
5. the energy consumption is low (compared to distillation).
6. vapour-liquid equilibria generally do not influence membrane properties.
7. no additional chemicals are needed (no pollution).
8. up-scaling is relatively easy to perform.

Some disadvantages and problems are:

1. the low transport rates through membranes.
2. the short life time of membranes.
3. the low chemical and/or thermal stability.
4. fouling and concentration polarization, reducing transport rate and separation characteristics.

History of membrane technology

Although membrane separation processes are only recently commercialized, membranes are actually not so very new. In all types of life on earth (plants, animals and humans) cells are surrounded by biological membranes, which form selective barriers for transport of specific materials, and control transport of heat and mass in living species. The first experiments with semipermeable membranes were performed using membranes of animal origin. According to Daubner [1.2] these experiments were performed by Reamur in 1714 [1.3]. In 1748 a study by Nollet was recorded [1.3], who observed the osmotic permeation of water into a vessel of wine, which was sealed with an animal bladder and was immersed in water. In 1803 Reuss was probably the first who performed systematic research on membrane phenomena [1.4]. A great contribution to membrane phenomena can be accounted to Fick, who published in 1855 [1.5] the phenomenological laws of diffusion (which are still being used nowadays to describe diffusional transport in membranes). Most research and observations on membrane phenomena in these early years concerned *natural* and *biological* membranes, usually originating from animals (bladders and skin). Because the membrane properties, such as pore size and porosity, of these membranes could hardly be influenced, *artificial* (man-made) membranes were developed. Actually, Fick was probably the first who prepared and studied some of the earliest artificial membranes, prepared from cellulose nitrate [1.3], also in 1855. Most research in those years concerned membranes based on cellulose nitrate; it was carried out on laboratory scale only, and was mainly aimed at biological applications.

A great step forward in membrane development became possible through the development of synthetic polymers, in the beginning of this century; especially from about 1940 on many new polymer membrane materials have been investigated. Examples of widely used *synthetic polymer* membranes are: poly(amides), poly(tetrafluoroethylene) (PTFE), poly(vinylidenefluoride) (PVDF), acrylic copolymers and cellulose acetate (CA). Although these new polymers provided better possibilities to influence the membrane formation properties (and thus the ultimate membrane properties), growth of already developed membrane separation processes to industrial scale was hindered by several factors: the low transport rates of the membrane processes (often diffusion controlled), compared to conventional separation processes; insufficient separation properties; lack of good membrane modules; low energy prices, favouring existing separation processes. It took until the development of asymmetric (skinned) cellulose acetate membranes (Loeb and Soerirajan [1.6]) before the first membrane separation process, desalination of brackish and seawater by reverse osmosis, could be commercialized on a large scale. The major breakthrough of this type of membrane is caused by the increase of transport rate through the membrane, without loss of selectivity. This new type of membrane consisted of a very thin, dense toplayer (<1 µm), supported by a relatively thick porous substructure (≈150 µm). The thin toplayer ('skin') determines the transport rate and the separation characteristics of the membrane, whereas the support is responsible for mechanical strength and should have no resistance for the permeating components. The preparation procedure applied by Loeb and Soerirajan was modified later to influence membrane properties, and membranes with different structures could be prepared for ultrafiltration and microfiltration processes. Because of better knowledge of the membrane formation process also other membrane processes, such as ultrafiltration, microfiltration and dialysis could be commercialized on a large scale. Some other, new membrane processes are being developed and commercialized at this moment, such as pervaporation and gas separation.

More complete reviews about the history of membrane technology have been published by Ferry [1.7], Teorell [1.8], Lakshminarayanaiah [1.9], Perry [1.10], Michaels [1.11] and Lonsdale [1.3].

Applications of membrane separation processes

The field in which membrane processes can be used is quite large, and is still expanding. The applications can be divided in *large scale* applications (industrial scale) and *small scale* applications. Examples of large scale applications are: the desalination of brackish and sea water, concentration of fruit juices, waste water treatment, oil/water separation, concentration processes in the diary industry, sterile filtration, recovery of helium from natural gas and dehydration of alcohols (pervaporation). Examples of small scale applications are: artificial kidneys, membrane lungs (oxygenators) and lab scale filtration. There are also some examples in which separation is not the main goal of the process: controlled drug release, applications in analytical chemistry, membrane sensors, pH-electrodes, battery separators, chlor-alkali cells and fuel cells. In table 1.1 a survey is given of most membrane processes now in use.

Membranes

Membranes can be classified in various ways, e.g. classification according to the kind of membrane (natural or artificial), the membrane material (polymeric or ceramic), the membrane structure (porous or dense), the cross section (symmetrical or asymmetrical, homogeneous or heterogeneous) or the method of preparation.

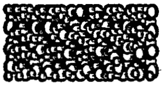
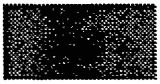
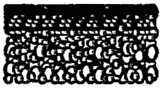
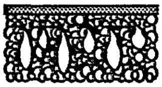
Table 1.1: Different types of membrane processes (L= liquid, V= vapour, G= gas).

membrane process	phases (feed/permeate)	applied driving force	applications
microfiltration	L/L	pressure	sterile filtration and removal of small particles from liquids
ultrafiltration	L/L	pressure	separation of macromolecular components from liquids
reverse osmosis	L/L	pressure	separation of low molecular weight components from liquids
thermo osmosis	L/L	temperature	separation of low molecular weight components from liquids and separation of liquids
dialysis	L/L	concentration	separation of macromolecular components from low molecular weight components (liquids)
electrodialysis	L/L	electric potential	removal of ions from liquids
piezodialysis	L/L	pressure	removal of ions from liquids
membrane distillation	L/L	temperature	separation of inorganic components from water
pervaporation	L/V	activity	separation of liquids
gas permeation	G/G	pressure	separation of gases
vapour permeation	V/V	activity	separation of vapour mixtures and removal of organic vapours from air
liquid membranes	L/L or G/G	concentration	removal of ions from liquids or separation of gases

A survey of these classifications is given in table 1.2, with some specific examples of commercial membranes. More details about the preparation techniques can be found in literature (see table 1.2 and [1.4]). For commercial applications generally asymmetric and composite membranes are preferred, because transport rates can be much higher compared to symmetric (porous and dense) membranes. Because for both types of membranes the membrane is partly or totally prepared by the phase inversion process, a great research effort in membrane research is devoted to the mechanism of membrane formation during the phase inversion process.

In laboratory studies however, dense membranes and symmetrical porous membranes are used as well, to investigate more fundamental aspects, such as the transport mechanism of membrane processes or the relation between the polymer structure and membrane properties.

Table 1.2: Schematic representation of different membrane types.

cross section	structure	preparation technique	commercial membranes
symmetrical	 cylindrical pores	track etching [1.12-1.14]	Nucleopore (polycarbonate)
symmetrical	 porous	sintering stretching [1.15-1.18]	GoreTex (PTFE) Amicon Celgard (PP)
symmetrical	 dense	casting [1.19]	
asymmetrical	 porous	phase inversion [1.20-1.26]	Accurel (PP) Millipore Sartorius
asymmetrical	 skinned (dense)	phase inversion [1.7,1.24-1.28]	Cellulose acetate
asymmetrical	 composite	coating [1.29-1.40]	NS-100, RC-100, FT-30, PA-300, PEC-1000 Monsanto, GFT

Transport through membranes

Separation processes generally are characterized by transport rate (or production rate) and the separation characteristics of the process. *Transport* through the membrane is achieved by applying a driving force over the membrane: this is the thermodynamic potential difference of one or more components over the membrane. This gradient in thermodynamic potential can be caused by gradients in pressure, temperature, concentration (or activity) or electrical potential, as given in table 1.1. *Separation* is achieved by differences in transport rates of the components through the membrane (for liquids and gases), or by rejection of one or more components by the membrane (for dissolved solids in liquids).

To describe transport through membranes, generally three mechanisms are considered: convective flow, diffusional flow and facilitated transport. Which type of mechanism should be used depends on the type of membrane. In some intermediate cases a combination of mechanisms could be operative.

Transport in *porous* membranes (see table 1.2) is generally described by convective flow (liquids or gases). Transport rates and separation are determined by molecular size, molecular weight and shape of the components (sieving), compared to the dimensions of the pores in the membrane. The separation properties are generally not influenced by the chemical nature of the membrane material. This *pore model* was developed by Schmid [1.41] and has later been improved by Mackay [1.42] and Meares [1.43]. Transport models for charged porous membranes were developed by Teorell [1.44] and Meyer et al [1.45].

In *dense* symmetrical membranes, *dense skinned* membranes and *composite* membranes transport is determined by solution and diffusion aspects of the components in the membrane. Transport rate and separation are determined by affinity and physico-chemical nature of the components, in relation to the polymer material. This so-called *solution-diffusion model* originates from Lonsdale et al [1.46].

In *liquid* membranes, which generally consist of a liquid immobilized in a porous membrane, transport of components is described by a *facilitated transport* mechanism. Transport rates and separation are determined by complexation of the components with a carrier, which is present in the liquid membrane phase.

Future perspectives of membrane separation processes

At this moment some membrane processes can compete with existing separation techniques. Although in principle membrane processes can replace conventional separation processes in some cases, a combination of conventional and membrane processes will generally lead to an optimized process design. The number of commercial applications is still increasing, and the prospects for the near future are quite good. In 1984 Drioli [1.47] estimated the average growth of the membrane market (in Europe) at about 12% per year. In many countries all over the world (USA, Japan and Europe) large research programs are initiated and supported by governments, mainly aiming at development and improvement of new membranes and processes. It can be expected that in the near future existing membrane processes will be optimized by availability of better membranes. The development of new membranes will be strongly directed at tailor-made membranes, for special separation problems. While until now mainly aqueous systems have been investigated, new membranes have to be developed for the separation of non-aqueous systems.

In the near future commercialization of some membrane processes, e.g. in the field of biotechnology (membrane reactors) and for liquid membranes can be expected, whereas commercial applications of gas separation and pervaporation will increase.

When the research described in this thesis was started in 1984, pervaporation was hardly commercialized. Although pervaporation already was explored about 25 years ago, the membranes showed insufficient properties to make the process commercially attractive. This thesis deals with the development of new pervaporation membranes, and with investigations on the transport mechanism; also some factors influencing the pervaporation performance of homogeneous membranes will be discussed.

1.3 Pervaporation

1.3.1 Introduction

Pervaporation is a membrane separation process that can be used to separate liquid mixtures. The liquid feed is brought into contact with a semi-permeable membrane, the permeate is removed as a vapour, but is usually condensed afterwards to obtain a permeate in liquid form.

Because liquids can not be separated using porous membranes, except for membrane distillation, pervaporation membranes have to be either fully dense membranes, or membranes that contain a dense toplayer (skinned or composite). The driving force for pervaporation is an activity gradient over the membrane, that is created by applying a low partial pressure of the permeating components at the permeate side of the membrane. This low partial pressure or low activity can be obtained by several methods:

1. using a vacuum pump and a condensor (creating a low total permeate pressure). The permeate is condensed before or after the vacuum pump. Whereas on laboratory scale the low partial pressure is determined by the vacuum pump, in commercial installations the temperature of the condensor (cooled by a cryostat) determines the downstream pressure. This pervaporation performance can be called: 'vacuum pervaporation'.
2. applying an inert sweep gas (e.g. N_2 [1.99] or air [1.49]). The permeate can be condensed, after which the inert gas is recirculated; the permeate containing sweep gas can also be vented. The name of this pervaporation performance is: 'sweeping gas pervaporation'.
3. applying an inert liquid [1.50]. The permeating components are diluted at the permeate side by an inert liquid. Because the inert liquid generally has to be recirculated, the permeate has to be separated from the permeate in a separate process, e.g. distillation. Although Cabasso

et al [1.50] called this process 'osmotic distillation', it can also be considered as 'perstraction'.

4. direct condensation of the permeate in the membrane cell: 'thermo-pervaporation' [1.51]. This is achieved by applying a low temperature interface near the permeate side of the membrane. The permeate is condensed against this cold wall, and has to be removed from the cell by gravitation.
5. using the permeate as a sweeping gas: 'continuous membrane column' [1.52].
6. using a non-wetted micro-porous membrane at the permeate side of the membrane and a cold liquid permeate [1.53]. After permeating through the dense membrane, the vapour permeates through the micro-porous membrane, and is condensed at the permeate side, which is kept at a lower temperature than the feed. The lower partial pressure of the permeating components is determined by the permeate temperature. In this case part of the liquid permeate can be recycled into the process directly, in contrast to method 3. The process can be called 'thermally driven pervaporation'. Whereas in this configuration a cold non-wetting liquid is applied to create a lower partial pressure, also direct vacuum or a sweeping gas can be used.

These different configurations of pervaporation are represented schematically in figure 1.3.

Pervaporation distinguishes itself from other membrane processes because of a phase transition, taking place during transport through the membrane. This means that at least the heat of evaporation of the permeate has to be supplied to the process. As a consequence pervaporation requires a higher energy input compared to other membrane separation processes, such as microfiltration, ultrafiltration and reverse osmosis. Therefore pervaporation will especially be attractive when the amount of the component that has to be removed is relatively small. Interesting possible applications are e.g. the separation of azeotropic or isomeric mixtures at a concentration near one of the pure components, the removal of small amounts of water from organic solvents [1.54] and the removal of relatively small amounts of organic contaminants from waste water streams.

Pervaporation has to compete with conventional liquid separation techniques, such as distillation, adsorption and extraction, or with other membrane separation processes, such as reverse osmosis. Because conventional techniques are difficult to replace, pervaporation will only be commercially applied on a large technical scale if it provides some very clear advantages compared to the conventional techniques. These advantages can be of technical, economical, or environmental nature. Pervaporation can compete with *distillation* in the case of the removal of the last small amount of one component, on the basis of a lower energy input of the process and lower investment costs. An additional advantage of pervaporation compared to *azeotropic distillation* is that no third component (entrainer) has to be added, which in azeotropic distillation has to be removed afterwards in a subsequent separation step.

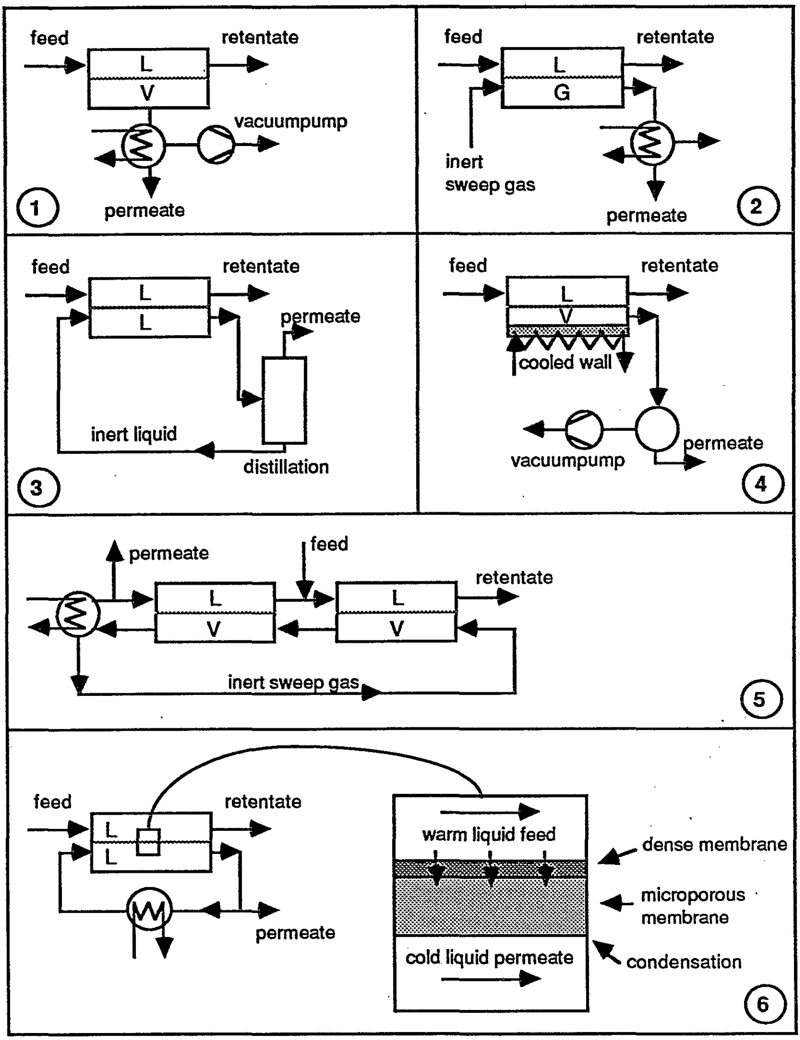


Figure 1.3: Schematic representation of different pervaporation configurations; 1=vacuum pervaporation; 2=sweeping gas pervaporation; 3=perstraction; 4=thermopervaporation; 5=continuous membrane column; 6=thermally driven pervaporation.

Another advantage of pervaporation is the flexibility and adjustability with respect to feed concentration and varying throughput. Because pervaporation is a continuous process, it can also provide advantages compared to extraction, which is usually processed batch wise; furthermore, extraction processes always needs two additional separation steps, for the purification of the raffinate phase and the extract phase (usually by distillation). Compared to reverse osmosis, pervaporation has the advantage that the osmotic pressure of the feed does not influence the process, which means that pervaporation can also be used at high concentrations of organic components in water; furthermore, generally higher separation characteristics are obtained using pervaporation. However, the required energy input for reverse osmosis can be lower, because no phase transitions occurs during permeation. When at low concentrations of the partly rejected organic components in water the osmotic pressure of the feed is relatively small, the fluxes in reverse osmosis generally are higher compared to pervaporation.

1.3.2 Historical development of pervaporation

The name of the process, which originates from *permeation* and *evaporation*, was first introduced by Kober [1.55] in 1917. This name however is somewhat confusing, because the properties of the membrane in pervaporation processes are not determined or influenced by the vapour-liquid equilibrium, as could be expected by the term 'evaporation'. In pervaporation it is even possible that a less volatile component permeates faster through a membrane compared to a more volatile component; a good example of this phenomenon is the preferential permeation of (the less volatile) water through hydrophilic polymer membranes from mixtures of water with (more volatile) methanol or ethanol. Another commonly used name in these early years was 'liquid permeation'.

It took until around 1960 before pervaporation became a subject of interest for many research groups. Especially the group of Binning and coworkers [1.56-1.59] reported on a number of possible chemical and petrochemical applications for this process. During these early years always homogeneous (non-porous) membranes were used. Unfortunately these membranes showed insufficient properties (permeability and selectivity) to compete with the usual separation techniques such as distillation and extraction; furthermore, the stability of the membranes needed improvements, and module design and materials were inadequate.

In the early seventies oil- and energy-prices suddenly raised to such an extent that alternatives for less energy-consuming separation techniques became of interest. Pervaporation turned out to be advantageous in two aspects. First, it could be used for the production of pure alcohol (from aqueous mixtures) as an alternative (renewable) liquid fuel. In the second place, it could be expected that, if better membranes were developed, pervaporation could also compete with distillation for other separation processes, regarding the energy-consumption of the separation process. This resulted in an increase in research for better membranes, and asymmetric [1.60] and composite [1.40] membranes were developed with thin dense toplayers. Although great effort was concentrated on the development of these asymmetric and composite membranes, homogeneous membranes are still being used to investigate transport phenomena (sorption and diffusion) for fundamental membrane research.

Uptill now a large part of the published work on pervaporation concerns the separation of *etha-*

nol/water mixtures. It took until 1982 before a commercial (composite) membrane was developed by the German firm GFT [1.40,1.61], for the dehydration of ethanol. These 'GFT membranes' consist of three layers: on top of a non-woven support a poly(acrylonitrile) ultrafiltration membrane is made, on which a very thin layer of crosslinked poly(vinylalcohol) is deposited by a coating technique. Later also other membranes of the same kind were developed, that could also be used for the dehydration of other organic liquids [1.62]. In the first commercial pervaporation installation in Brasil [1.61] this type of composite membranes was assembled in a plate-and-frame module. The pervaporation installation was combined with a distillation plant for the production absolute ethanol from a fermentation broth.

Another type of membranes that turned out to have excellent dehydration properties are ion-exchange membranes [1.63-1.66]. Especially by changing the positive counter-ion the properties could be improved to a large extent. A general drawback of this type of membranes is the (long term) instability, due to washing out of the counter-ion. After some time the positive ion is exchanged by a proton (from the aqueous feed), in which case the separation properties generally decrease strongly. In that case the membranes have to be regenerated periodically.

At this moment pervaporation is used on a small scale in analytical chemistry for the removal of traces of water from organic solutions [1.67] and for the determination of alcohols in fermentation broths [1.68]. A large scale application [1.61,1.62] is the dehydration of organic liquids (azeotropic mixtures in some cases). Other possible separation problems that can be encountered by pervaporation at this moment are [1.69]:

- final dewatering of organic solvents (e.g. methylene chloride; chloroform),
- dehydration of solutions (e.g. fruit juices; kerosene),
- dehydration of multi-component mixtures (e.g. ethanol/toluene/isopropanol/water; ethanol/ethyl ester/methyl ester/water),
- removal of organics from aqueous streams (e.g. phenols; chlorinated hydrocarbons; solvents),
- removal of alcohols from fermentation broths and de-alcoholization of beer and wine.

1.3.3 Mass transfer during pervaporation

As for most membrane processes, pervaporation membranes are characterized by the transport rate through the membrane and the separation performance. For pervaporation usually the *transport rate* is represented by the *flux J*: the amount of liquid that is transported through the membrane per unit membrane area per unit of time. Until now no standardization of the unit of flux is proposed, which leads to a large variety of units reported in literature: cm/h (cm^3/cm^2h), l/m^2h, kg/m^2h, g/cm^2s, kg/m^2d, $mole/m^2s$, gfd (gallons per square feet per day). Because the permeate is a vapour, and the permeate density is dependent on temperature, mass or molar fluxes should be preferred. Other investigators use permeabilities (mole.m/m^{2}s.Pa) to characterize the transport rate, or the product of flux and membrane thickness: J.l (cm^3.cm/cm^2.s; µm.l/m^{2}h).

Also for the *separation* performance of pervaporation membranes different parameters are used. In fact all parameters are mathematically calculated from the concentrations of the components (A and B) in the feed (c_A^f and c_B^f) and in the permeate (c_A^p and c_B^p). Unfortunately no standardization of nomenclature for the separation parameters is proposed yet, leading to confusing terms in literature, such as 'selectivity', 'separation factor' and 'enrichment factor'. These terms are not always used consistently; the most common combinations of nomenclature and definition are given below.

The most commonly used parameter is the *selectivity* α; it is defined by equation (1) [1.70-1.72]. In some cases this parameter is denoted by $S_{A/B}$ [1.72].

$$\alpha_{A/B} = (c_A^p/c_B^p)/(c_A^f/c_B^f) \qquad (1)$$

Another parameter is the *separation factor*, which is calculated according to equation (2) [1.74, 1.75]:

$$\beta_{A/B} = c_A^p/c_A^f \qquad (2)$$

In both cases component A is the preferentially permeating component from the A/B mixture.

Finally, some investigators [1.75,1.76] separate the pervaporation selectivity α^p into an evaporation selectivity α^{evap} (relative volatility) and a 'membrane selectivity' α^m:

$$\alpha^p = \alpha^{evap} . \alpha^m \qquad (3)$$

Although this can be useful for the comparison between distillation and pervaporation, it is somewhat misleading, because it suggests that the pervaporation selectivity is influenced by the relative volatility of the components.

Transport of low molecular weight compounds in dense (non-porous) polymer membranes is generally described by the so-called *solution-diffusion model*. This model, developed for transport of water and salt in reverse osmosis membranes [1.46,1.77] is also widely accepted to describe transport of liquids in dense polymer membranes (or in dense toplayers of skinned and composite membranes) during pervaporation.

According to this model the pervaporation selectivity is obtained by a combination of selective sorption of the components in the membrane and selective diffusion through the membrane; the desorption of the components out of the membrane is so relatively fast, that it does not influence the flux and selectivity. The overall permeation rate (flux) is assumed to be determined by diffusion in the polymer only. Because sorption and desorption can be considered and described by the same process, for fundamental studies usually only diffusion and sorption phenomena are considered. For asymmetric membranes capillary condensation of the permeate in the porous support can influence the desorption step.

Diffusion

Diffusion of low molecular weight components in polymers is generally described by the diffusion law of Fick. Although this law has been developed for diffusion in elastomeric polymers, it is also widely used to describe transport in glassy polymer membranes during pervaporation. Diffusion in glassy polymers is actually very complicated, due to phenomena such as stress relaxation, and time and concentration dependency of diffusion coefficients. Because the results obtained by using Fick's law are quite satisfactory for the description of permeation through glassy polymer membranes as far as single component transport is concerned, this simple relation is still being used now. According to this relation the transport rate of a component i (J_i) is proportional to the gradient of the concentration (c_i^m) of this component in the polymer (in chapter 2 another approach is used, finally leading to the same equation):

$$J_i = - D_i \,.\, dc_i^m/dx \qquad (4)$$

The proportionality coefficient is the diffusion coefficient, which in many cases is dependent on the concentration of the components in the membrane. In literature many mathematical functions have been proposed for this concentration dependence, which in some cases are based on a physical or mathematical model. Because in the case of a binary liquid mixture of components i and j the diffusion rate of component i can be dependent on the concentrations of both i and j, so-called 'thermodynamic coupling coefficients' can be introduced (A_{ii}, A_{ij}).

a) Constant diffusion coefficient: $D_i = D_i^o$.

This is the most simple equation, that can only be used in the case of extremely low concentrations in the membrane. This description was used by Lee [1.78].

b) Linearly dependent diffusion coefficient: $D_i = D_i^o . (A_{ii}.c_i^m + A_{ij}.c_j^m)$.

This type of relation was used by Albrecht [1.73] and Greenlaw et al [1.79,1.80]. In most cases

A_{ii} was taken equal to 1; for A_{ij}=0 this relation describes non-coupled diffusion.
Shelden et al [1.81] also used a somewhat more complicated form of this equation, which can be transformed into: $D_i = D_i^o + (A_{ii}.c_i^m + A_{ij}.c_j^m)^{Ki}$; Ki was taken 0.5, 1 or 2.

c) Exponentially dependent diffusion coefficient: $D_i = D_i^o.\exp(A_{ii}.c_i^m + A_{ij}.c_j^m)$.
This is probably the only relation based on a physical background (the 'free volume theory' [1.82-1.85]) and it is used by most investigators [1.86-1.92].

d) $D_i = D_i^o.(1 - A_i.c_i^m)^{-2}$.
This relation [1.93] has never been used for description of permeation experiments.

Whereas according to most relations the diffusion coefficient increase with increasing concentration, it is also possible that the diffusion coefficient decreases. This can be the case when the diffusing component can form clusters due to strong intermolecular hydrogen bonding (e.g. water [1.94]).

If the concentrations in the membrane can be related to the concentration in the bulk feed and to the permeate pressure, integration of equation (4) results in an equation for the pervaporation flux; the pervaporation selectivity can be obtained from the ratio of the component fluxes [1.73, 1.78,1.86-1.92].

The approach given here, to take into account the effect of mutual interactions of the components on the diffusion of a given component, is a very general one, which is used by many investigators. Another approach originates from irreversible thermodynamics. According to this theory the flux of a component i through a membrane is a result of the driving force for the component i itself, and of the driving force for the other component:

$$J_i = L_{ii}.d\mu_i^m/dx + L_{ij}.d\mu_j^m/dx \qquad (5)$$

In this equation L_{ij} represents a '*flow coupling coefficient*'. To distinguish between coupling of flows (according to equation (5)), and the coupling phenomena expressed by equation (4) when D_i and c_i^m depend on the concentration of all components present, we use the term 'thermodynamic coupling' for coupling phenomena in diffusion or sorption.

Sorption

Sorption of liquids in polymers can be divided in sorption of pure liquids and sorption of liquid mixtures. In the solution-diffusion model it is assumed that sorption of the components at the membrane interface at the feed side can be considered as a thermodynamic equilibrium. Therefore, in the case of a pure liquid the concentration in the membrane can be calculated from a single swelling experiment. The solubility in the membrane can be predicted using Flory-Huggins thermodynamics [1.95] (see chapter 2 of this thesis).

In the case of sorption of a liquid mixture, the description is more complicated. Although most investigators [1.72,1.78,1.96] assumed that both components absorb independently (i.e. only dependent on the pertinent concentration in the feed), the sorption of component i in the polymer will generally be dependent on both the concentrations of the components in the feed and the concentration of component j in the polymer. This thermodynamic coupling effect will especially occur for a mixture of two strongly interacting components, such as ethanol and water.

Whereas most investigators [1.97,1.98] used empirical mathematical expressions to take into account the thermodynamic coupling, Mulder et al [1.99] used relations derived from Flory-Huggins thermodynamics, to describe sorption of ethanol/water mixtures in homogeneous cellulose acetate, poly(acrylonitrile) and poly(sulfone) membranes. Although the agreement between experiments and theoretical results could only be obtained by introducing additional parameters, this approach is preferred for the prediction of sorption properties of liquid mixtures in polymers.

Permeation

Due to thermodynamic coupling phenomena (both in sorption and in diffusion) membrane properties for binary mixtures can not be predicted on the basis of pure component data. The membrane properties have to be described by a mathematical combination of relations for diffusion and sorption of liquid mixtures in the polymer material. According to the solution-diffusion model the diffusion step is the rate determining step in the transport mechanism (sorption-diffusion-desorption); the fluxes of the components will then be proportional to the reciprocal thickness of the membrane (see equation 3). This implies that fluxes through homogeneous membranes can be increased by decreasing the membrane thickness. The selectivity is independent of membrane thickness, because the fluxes of both components depend on the thickness in the same way. This expected behaviour (according to the solution-diffusion model) of flux and selectivity as a function of membrane thickness is presented schematically in figure 1.4.

Although in some cases this model seems to be appropriate, deviations from this model have been reported in literature.

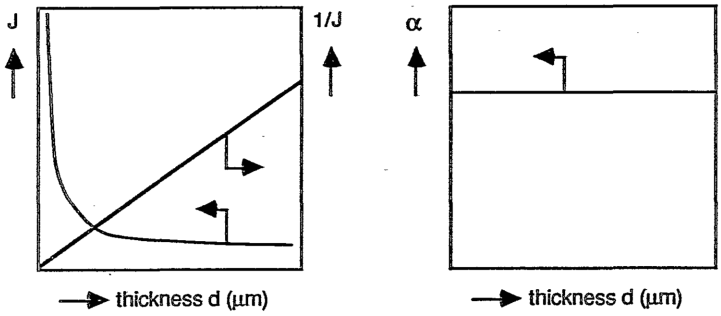


Figure 1.4: Flux and selectivity for homogeneous membranes, as a function of the membrane thickness, as predicted by the solution-diffusion model.

1.3.4 Influence of different parameters on pervaporation performance

In the previous paragraph the commonly used solution-diffusion model was described. Because experimental deviations from this model have been found, there must be some more factors determining the performance of pervaporation membranes. In this subparagraph a general overview will be given of factors that influence the pervaporation performance using homogeneous membranes. Some of these factors can explain deviations from the solution-diffusion model, some caused by the membrane, and some others caused by the process conditions.

1.3.4.1 Factors determined by the membrane

Polymer material

The starting point of the development of pervaporation membranes is the polymer material, because this is the most important factor, determining the final membrane properties. A polymer material must be selected on the basis of the following aspects:

1. The polymer material must be resistent to the components of the feed that have to be separated.
2. The polymer must be suitable for the desired membrane preparation methods (see table 1.2).
3. The polymer membrane must provide appropriate chemical, thermal and mechanical stability.
4. The expectation for permeation properties must be good, on the basis of solution and diffusion aspects.

Whereas in this paragraph a summary will be given of the factors that can influence the pervaporation properties of homogeneous membranes, the most important factor is the choice of the polymer material. To demonstrate the great variety of pervaporation properties that can be obtained for a given separation problem using different polymers as a membrane material, in table 1.3 the normalized flux (to 10 µm membrane thickness) and the selectivity (for water) for the separation of ethanol/water mixtures are given.

Table 1.3: Pervaporation properties of homogeneous membranes from different polymer materials. Feed: ethanol/water mixture, 20-30°C.

polymer	type	interaction	c_e^f (w% eth)	J_{10} (kg/m^{2}h)	α (-)	reference
Poly(acrylonitrile)	glassy	hydrophilic	50	0.012	650	this work
Poly(vinylalcohol)-100%	glassy a)	hydrophilic	90	0.021	440	[1.101]
Poly(acrylamide)	glassy a)	hydrophilic	90	0.55	190	this work
Cellulose acetate	glassy a)	hydrophilic	50	1.36	4.2	[1.100]
Poly(sulfone)	glassy	hydrophobic	50	0.008	330	[1.100]
Poly(phenylene oxide)	glassy	hydrophobic	50	0.08	23	this work
Poly(dimethylsiloxane)	rubber	hydrophobic	50	0.17	0.3 b)	[1.100]
PTMSP c)	glassy	hydrophobic	50	0.3	0.25 b)	[1.102]

a) probably in the rubbery state during pervaporation; b) preferential permeation of ethanol; c) PTMSP= poly[1-(trimethylsilyl)-1-propyne]

By variation of the polymer the membrane permeates water or ethanol preferentially, extremely high or low selectivities, and low or high fluxes are found. It is clear that the pervaporation properties are strongly related to the physico-chemical properties of the polymer, such as hydrophilicity, possibilities for hydrogen bonding, polar interactions or other specific interactions between the polymer and the permeating components. However, these structure-property relationships are not always very clear: an illustrative example is that although both PSf and PPO are hydrophobic polymers (preferential permeation of ethanol is expected), water permeates preferentially.

Membrane thickness

From the solution-diffusion model it can be concluded that the pervaporation flux is proportional to the reciprocal membrane thickness (see equation (4)), assuming that diffusion is the rate-determining step. This has been confirmed by several investigators [1.58,1.103]. Deviations of this reciprocal relationship can be expected, if diffusion through the polymer membrane is not the rate-determining step. Some experimental results of these deviations have been published in literature ([1.104]; [1.105], assigned to concentration polarization); also an increase of selectivity with increasing thickness has been found [1.103,1.104]. In figure 1.5 an example is given, to illustrate the decrease of selectivity as a function of the membrane thickness, for an extremely selective polymer membrane for the dehydration of ethanol/water mixtures.

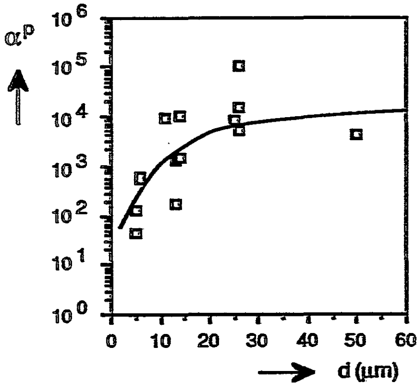


Figure 1.5: Pervaporation selectivity for homogeneous poly(acrylamide) membranes for the dehydration of ethanol/water mixtures, as a function of the membrane thickness.
Feed: 90 w% ethanol, 70°C.

Deviations of the expected reciprocal relationship between flux and membrane thickness can also be due to some of the other aspects discussed in this subparagraph; some of these aspects will be discussed in more detail in chapter 4.

Artefacts

Artefacts originating from membrane manufacture can also have an influence on pervaporation results. These effects will be more likely to occur and will be stronger for thin membranes, leading to a strong decrease of the selectivity and an increase of flux. Artefacts in membranes can be due to contaminants in the basic polymer material (dust particles, pollutants) or can originate from the evaporation step of the solvent during the membrane preparation. The effect of artefacts can be decreased if the casting solution is filtered before use, and the evaporation step is carried out in a clean environment ('clean room').

Sorption resistance

If the sorption of the components into the membrane at the feed side is not in thermodynamic equilibrium, a sorption resistance can be defined. In the solution-diffusion model the diffusion step is assumed to be the rate-determining step. For high diffusion rates (e.g. for decreasing membrane thicknesses) the sorption of the components (independent of thickness) into the membrane can also influence the transport rate through the membrane. This means that the sorption in the steady-state during pervaporation is lower than in equilibrium, and a step function in activity at the membrane interface occurs. This results in deviations from the linear relationship between flux and reciprocal membrane thickness.

A mathematical model that takes into account a sorption resistance at the membrane interface was reported by Sieh et al [1.106], and was tested by dialysis experiments.

The phenomenon of a sorption resistance has generally been neglected, because no physical interpretation is found yet. A concentration step has been found experimentally [1.86,1.91, 1.107], in which cases the equilibrium sorption value for the components in the polymer was higher than the concentration at the membrane interface at the feed side during pervaporation. This sorption resistance will generally lead to lower fluxes, especially for thinner membranes; the selectivity can both increase or decrease in case of a sorption resistance.

Membrane morphology

The morphology of polymer membranes is mainly determined by the choice of the polymer material and by the membrane preparation method. Although for a given polymer the most pronounced difference in morphology is the difference between porous and dense (non-porous) membranes, even in the case of the preparation of homogeneous dense membranes the morphology can be dependent on the preparation method.

Homogeneous membranes are generally prepared by casting a viscous polymer solution on a solid support, followed by evaporation of the solvent, usually in an inert atmosphere. An important factor is whether the polymer used is *amorphous* or *semi-crystalline.*

For amorphous polymers the rate of evaporation of the solvent determines to a large extent the permeation properties of the membrane. This rate of evaporation can be influenced by the evaporation temperature, the type of solvent (volatility), and can be adjusted further by partial saturation of the atmosphere by solvent vapour. It can be expected that higher evaporation rates result in a less dense structure of the membrane, leading to higher fluxes. Also the arrangement of the functional groups (interacting with the permeating components) can be dependent on the evaporation rate, resulting in a change of selectivity. These aspects are discussed in more detail, in relation to a specific problem, in chapter 4.

For a semi-crystalline polymer the rate of evaporation can also influence the crystallinity of the membrane [1.108]. Because crystallization is a time-dependent process the rate of evaporation determines the growth of the crystallites. Not only the total amount of crystallinity can be influenced, but also the size and shape of the crystallites can depend on the evaporation rate.

Because crystallites can be considered as physical crosslinks and are impermeable to liquids, both diffusion and sorption will depend on crystallinity [1.87,1.109-1.113]. It can be expected that high crystallinity (small crystallites) leads to higher selectivity and smaller fluxes. If the crystallites become too large, or the overall crystallinity too high, artefacts can occur, leading to a decrease in selectivity.

Because the morphology of a membrane can be dependent of the evaporation rate (or time), it is expected that thin membranes have a different morphology compared to thick membranes. It is even possible that the morphology of thick membranes is dependent on the place in the membrane: during evaporation a concentration profile of the solvent will occur in the casted film. The concentration of the solvent at the film surface in contact with the air or nitrogen atmosphere is relatively low, whereas the opposite surface (in contact with the solid support) remains longer in the totally solvent-swollen state, resulting in a different morphology. These effects can lead to deviations from the solution-diffusion model: selectivities depending on the thickness, and fluxes being not proportional to the reciprocal membrane thickness.

Once a membrane has been prepared (by evaporation of the solvent), the morphology can still be influenced by some factors. The first factor is time. Time-effects can be divided into short term and long term effects. The short term effects originate from the build-up of the concentration-profile in the membrane after starting a pervaporation experiment. If started with a dry membrane, the membrane will swell (mainly at the feed side) during the pervaporation process, leading to an increase of flux. If the membrane was pre-swollen before the experiment, the membrane deswells (mainly at the permeate side), leading to a decrease of the flux. The time needed to reach steady-state generally increases with decreasing permeation rate of the components. Relaxation phenomena are long term effects, generally taking place in glassy polymers. Relaxation of the polymer can take place during the pervaporation process, and will lead to a more dense structure, resulting in a decrease of flux (see chapter 4). In a semi-crystalline polymer the crystallization can be a function of time, also leading to a decrease of flux.

Finally, the morphology can also be influenced by a pre-treatment of the membrane. The most common pre-treatments are: heat-treatments (curing) [1.114,1.115] or the use of swelling agents. Elyassini et al [1.74] showed the influence of the nature of the swelling agent (concentration of ethanol/water mixtures) on the ultimate pervaporation characteristics of poly(vinylalcohol) membranes for the dehydration of ethanol/water mixtures.

1.3.4.2 Factors determined by the process conditions

Feed concentration

According to the solution-diffusion model the properties of pervaporation membranes are determined by sorption and diffusion of the components in the membrane. Because generally both sorption and diffusion phenomena of a liquid in polymers are dependent on the composition of the liquid mixture, also the permeation characteristics will be dependent on the feed concentration.

Feed pressure

In most membrane processes (microfiltration, ultrafiltration, reverse osmosis and gas permeation) the membrane characteristics are strongly dependent on the feed pressure: generally the flux increases with increasing feed pressure, because of an increased driving force over the membranes. For pervaporation the main contribution to the driving force (gradient of the thermodynamic potential) is caused by the activity gradient of the components in the membrane, as can easily be demonstrated by thermodynamic considerations [1.78]. The maximum gradient is obtained for zero permeate pressure: $P_p \rightarrow 0$; this can be compared with reverse osmosis (RO) at infinite feed pressure: $P_f \rightarrow \infty$. Lee [1.78] showed theoretically that unrealistic high transmembrane pressures in RO have to be applied, to get the same flux and selectivity compared to pervaporation (at moderate permeate vacuum pressures). This was confirmed by experimental results reported by Thompson et al [1.79-1.81, 1.116-1.118]. Also their mathematical model predicted that in case of low permeate pressure the feed pressure has only a relatively very small effect on the pervaporation performance. Only for higher permeate pressures (pressures approaching the saturation pressure of the permeate $P_p^o = \Sigma \gamma_i . x_i . P_i^o$) the feed pressure influences the pervaporation characteristics significantly.

Permeate pressure

Because the permeate pressure is directly related to the activity of the components at the permeate side of the membrane, the permeate pressure has a strong influence on the pervaporation characteristics. The maximum driving force is obtained at zero permeate pressure; increase of permeate pressure results in a decrease of driving force, and the flux will decrease. This was described mathematically and confirmed by experiments from Thompson et al [1.79-1.81, 1.116-1.118] and from Spitzen [1.97]. If the permeate pressure is equal to the saturation pressure of the permeate (at the temperature of the feed), the activity gradient is zero, leading to a strong decrease in flux, according to only a small pressure gradient over the membrane. Also the selectivity is dependent on the permeate pressure. The selectivity can increase or decrease at increasing permeate pressure, depending on the relative volatility of the permeating components. At the saturation pressure of the permeate ($P_p^o = \Sigma \gamma_i . x_i . P_i^o$) the pervaporation selectivity will only be determined by the relative volatility of the permeating components.

So, in general the overall pervaporation characteristics decrease with increasing permeate pressure. This is a very important aspect for practical applications, because in large technical installations the permeate pressure usually will be higher than in laboratory set-ups; it is mainly determined by the temperature of the condenser. Another factor, that determines the effective permeate pressure, is the porosity of the membrane support. Because the membrane characteristics are determined by the local pressure at the surface of the active layer of the membrane, a pressure drop over the porous support will lead to smaller activity gradients of the components in the active membrane, resulting in a deterioration of pervaporation characteristics [1.119], especially for asymmetric and composite membranes.

Concentration polarization

Due to permeation of the feed components through the membrane, the liquid composition in the boundary layer at the membrane surface may change. Because one component is preferentially transported through the membrane, a concentration gradient will occur near the membrane wall: the concentration of the preferentially permeating component i drops from $c_1 \rightarrow c_2$ (see figure 1.6). This phenomenon is called concentration polarization; and it is described in more detail in chapter 6 of this thesis. Concentration polarization can be influenced by the mixing conditions in the feed. Although most investigators generally neglect this phenomenon, experimental evidence of the influence of mixing conditions has been reported in literature [1.120-1.123].

Additives to the feed

The pervaporation characteristics can strongly be influenced by addition of certain components to the feed mixture. Heisler et al [1.124] studied the addition of solutes on the separation performance of ethanol/water mixtures by cellophane membranes. By addition of different solutes to the feed the pervaporation selectivity for water could be either increased or decreased, while the flux was influenced in the opposite direction.

Temperature effects

Because sorption and diffusion of low molecular weight components in polymers are generally dependent on temperature, also the permeation characteristics are dependent on temperature. Since diffusion rates in polymers are increasing with increasing temperature, also permeation rates increase with increasing temperature. The selectivity is not so strongly dependent on the temperature: in most cases a small decrease of selectivity is found at increasing temperature.

The temperature that determines the permeation characteristics is the temperature of the membrane itself, which is mainly determined by the temperature of the liquid feed mixture. In pervaporation a phase transition occurs during transport of the components through the membrane: the feed is a liquid, whereas the permeate is removed as a vapour. The heat of evaporation of the permeate has to be supplied to the membrane, mostly from the feed. Two heat transfer steps can be distinguished, generally leading to a temperature drop from the bulk feed to the bulk permeate. The first step is convective heat transport from the bulk feed towards the membrane surface at the feed side. This leads to a temperature gradient in a boundary layer at the feed side of the membrane, and is called 'temperature polarization'. This heat transport is determined by the heat transfer coefficient at the feed side. An increase of the convective feed flow parallel to the membrane surface, or stirring of the feed mixture, will reduce the temperature drop in the boundary layer.

The second step is conductive heat transport through the membrane. This leads to a temperature gradient in the membrane, which determines the actual membrane properties. This heat transport is determined by the heat conductivity of the (partly swollen) membrane. The temperature level in the membrane is also determined by the convective heat transport in the boundary layer at the feed side of the membrane.

The overall heat transport required is determined by the flux and the heat of evaporation of the permeate.

Both effects mentioned before (temperature polarization and temperature gradient in the membrane) lead to a lower average membrane temperature, resulting in a change of flux and selectivity. Nagy et al [1.115] and Rautenbach et al [1.119] have reported on experimental temperature drops from the bulk feed to the bulk permeate. Gooding [1.125] showed by calculations that it is possible that the overall temperature drop from the bulk feed to the permeate side of the membrane is only determined by the temperature drop in the boundary layer at the feed side.

1.3.4.3 Overall transport mechanism for pervaporation

If the solution-diffusion model is combined with the factors described above, several steps can be distinguished in the overall transport mechanism. These steps can be demonstrated by the concentration profile (and the activity profile) of one component transported from the bulk feed to the bulk permeate, as is given in figure 1.6.

1. Concentration polarization on the feed side of the membrane. This process is described by diffusion of the components in the boundary layer near the membrane. The concentration of the preferentially permeating component drops from $c_1 \rightarrow c_2$ ($a_1 \rightarrow a_2$).
2. The components are absorbed into the polymer membrane. This process is described by a thermodynamic equilibrium: $c_2 \rightarrow c_3$ ($a_2 = a_3$).

3. If equilibrium sorption is not reached, a sorption resistance can be defined. This results in a concentration step at the membrane interface: $c_3 \rightarrow c_4$ ($a_3 \rightarrow a_4$).
4. The components diffuse through the membrane according to a concentration gradient in the membrane: $c_4 \rightarrow c_5$ (actually an activity gradient: $a_4 \rightarrow a_5$).
5. The components desorb out of the membrane, according to a thermodynamic equilibrium: $c_5 \rightarrow c_6$ ($a_5 = a_6$).
6. If in the desorption step a thermodynamic equilibrium is not reached, a desorption resistance can be defined. A concentration (or activity) drop at the membrane interface occurs: $c_6 \rightarrow c_7$ ($a_6 \rightarrow a_7$). This can be considered as a slow evaporation of the components into a vapour phase.
7. Finally it is possible that, due to pressure losses at the permeate side of the membrane or hindered removal of the permeate (piping; membrane support), the concentration (or activity) at the membrane surface is higher than the concentration (or activity) that is determined by the applied driving force: $c_7 \rightarrow c_8$ ($a_7 \rightarrow a_8$).

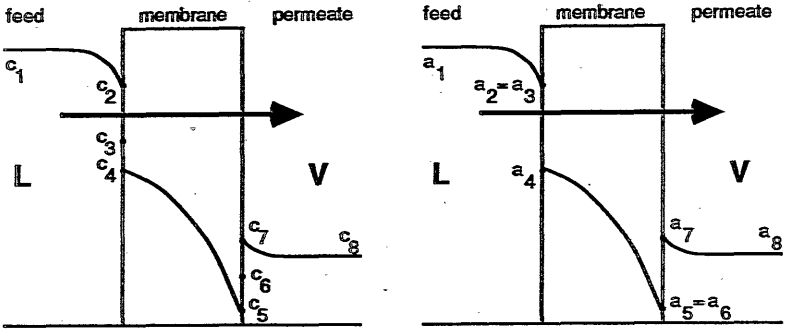


Figure 1.6: Concentration and activity profile of the preferentially permeating component, during transport from the bulk feed to the bulk permeate for pervaporation membranes (not on scale).

This total transport mechanism is a very general one. Whereas in practical applications step 1 generally can be of some importance (because of non-ideal mixing conditions), during laboratory experiments this step can easily be avoided or neglected. In the case of permeation of pure liquids, this step does not exist. Only a temperature gradient remains in that case. Furthermore, steps 3 and 6 are generally neglected also, although some indications for the presence of a sorption resistance (step 3) have been reported in literature [1.86,1.91,1.107]. The effect of step 7 generally can be decreased by a better module design.

The three remaining steps (2, 4 and 5) represent the commonly used transport mechanism for pervaporation: solution, diffusion and desorption *(solution-diffusion model).*

If all factors influencing the performance of pervaporation are considered, it is clear that it is provocative to speak about intrinsic properties of polymer membranes (flux and selectivity). Because membrane manufacturing is influenced by so many factors, it is rather difficult to prepare reproducible membranes. If the influence of one parameter on the membrane characteristics is to be investigated, it can be expected that also some other factors are influenced, which makes comparison of the membrane properties extremely difficult.

1.3.5 Pervaporation of ethanol/water mixtures

Although the separation of various liquid mixtures by pervaporation has been investigated [1.126,1.127], most research efforts concentrate on the separation of azeotropic liquid mixtures, especially aqueous alcohols (iso-propanol and ethanol). The main interest in these latter separation problems originates from a possible replacement of the energy-consumptive azeotropic distillation. Whereas iso-propanol and ethanol are important basic chemicals in the chemical industry, they can also be used as an alternative, renewable energy source. For instance, by fermentation of biomass aqueous ethanol (about 5%) can be obtained, which for practical applications has to be concentrated. Although in the first concentration step (up to about 70-80% ethanol) pervaporation can not compete with distillation yet, in the last dehydration step azeotropic distillation can be replaced by pervaporation [1.61]. After an intensive research was started for the development of membranes for dehydration purposes, later also membranes were developed for the preferential permeation of ethanol (mainly silicone-based membranes). At this moment these last types of membranes show insufficient flux and selectivity to make the process competitive with normal distillation, although some real improvements have been made recently by using alcohol selective zeolites in silicone rubber membranes [1.128]. In this thesis only membranes for dehydration of ethanol/water mixtures will be considered.

Also other membrane processes have been investigated for the separation of ethanol/water mixtures: membrane distillation [1.129-1.131], reverse osmosis [1.132-1.134] and vapour permeation [1.135]. Membrane distillation can only be used at low ethanol concentrations in the feed, because the microporous membrane should not be wetted by the feed solution. The separation that can be obtained is only determined by the relative volatility of the feed mixture; hence, ethanol permeates preferentially. In reverse osmosis of ethanol/water mixtures ethanol is partly rejected by the membrane. It can only be used at low ethanol concentrations in the feed; at higher ethanol concentrations the high osmotic pressures of the feed solution will decrease the driving force for transport. Furthermore, the experimental retention values for ethanol are rather low. Vapour permeation is a relatively new technique, that can provide advantages compared to pervaporation if the feed is already in the vapour phase, like it is when distillation is used as a first concentration step.

For the dehydration of ethanol/water mixtures a lot of polymers have been screened as a membrane material. Generally a membrane with a high flux gives a low selectivity, and vice versa. To develop membranes with an optimal combination of flux and selectivity two strategies can be followed. If one starts with a highly *selective* membrane material, the flux can be improved by decreasing the effective membrane thickness and by increasing the feed temperature. If a highly *permeable* polymer material is selected, the selectivity can be increased e.g. by chemical modification or by crosslinking.

The best results for dehydration of ethanol/water mixtures have been obtained with membranes preprared from hydrophilic polymers (usually water soluble) [1.66], such as poly(vinylalcohol) membranes [1.40,1.101,1.136,1.137] and by charged membranes [1.63,1.64,1.66]. As mentioned before, the main problem with this last type of membranes are the long term flux and selectivity, due to washing out of the counter-ion (which give these membranes the good separation properties).

In table 1.4 some pervaporation results are given for some polymers that were screened as a membrane material. This table shows that the best membranes (combining a high selectivity with a reasonable flux) are obtained with water-soluble polymers.

Table 1.4: Pervaporation results for ethanol/water mixtures with homogeneous membranes; fluxes normalized to 10 μm thickness. Feed: 90 w% ethanol, 70°C.

polymer	membrane thickness (μm)	J_{10} (kg/m^{2}h)	α (-)
Poly(acrylonitrile)	56	0.036	12500
Poly(acrylonitrile)	22	0.022	3000
Poly(acrylonitrile-co-methacrylate)	18	0.020	4100
PVA (98%) *(after heat-treatment)*	65	0.182	350
PVA (98%) *(crosslinked)*	41	0.402	106
PVA (100%) *(crosslinked)*	39	0.30	140
Poly(acrylic acid) - H^+	38	8.74	6.2
Poly(acrylic acid) - Cs^+	33	1.29	56
Poly(ether imide)	15	0.12	52
Poly(ether sulfone)	24	0.36	52
Poly(hydrazide)	20	0.66	19
Poly(acrylamide)	50	0.055	4080
Poly(acrylamide) low carboxyl content	50	0.11	2950
Poly(acrylamide) high carboxyl content	60	0.50	2200

1.3.6 Future perspectives of pervaporation

The future perspectives for pervaporation are quite promising. Since the development of the first commercially available membrane in 1982 the market for pervaporation has increased strongly. This is demonstrated in figure 1.7, in which the total capacity of installed pervaporation installations is given since 1982 [1.138]. According to some estimations the total market potential for pervaporation will reach about US $ 100 million per year in 1990, with an increase of 20%-30% per year [1.69]. According to other (non-official) rough estimations the expected market potentials in 1995 are between US $ 800 and $1000 million.

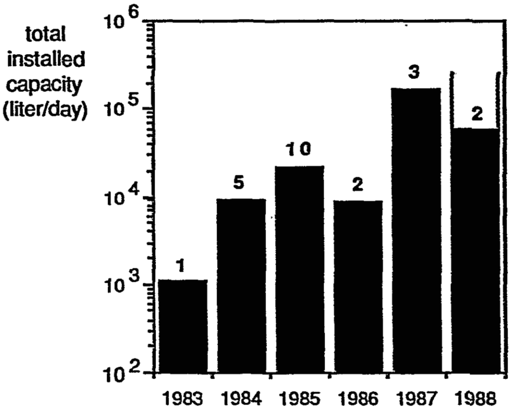


Figure 1.7: Worldwide total installed capacity of pervaporation plants [1.138]; (the numbers indicate the number of installed plants). The results for 1988 are updated to May 1988.

The commerciallization of pervaporation started in Europe: GFT (Germany), SETEC (The Netherlands), Lurgi (Austria) and Vogelbusch (Austria), and more recently Carbone Lorraine (France). At this moment also in the USA (Bakish Materials Corp. and MTR Inc.) and in Japan (Mitsui Engineering Co.) pervaporation installations are available.

It is expected that in the near future membrane development will aim at more difficult separation systems, such as the separation of non-aqueous liquids (e.g. aliphatic/aromatic and isomeric mixtures) and the dehydration of aliphatic organic acids (e.g. acetic acid, formic acid). Another interesting application that is under investigation now, is the removal of small amounts of volatile organic contaminants from ground water or waste water. A more complete review on possible applications for pervaporation in the next 10 years has been reported by Tusel [1.69].

Whereas nowadays the commercial membranes can be used for more than one system (e.g. the GFT membrane for the dehydration of different organic liquids) these more difficult separation problems will probably lead to the development of tailor-made membranes. Because these applications concern more aggressive feed solutions, new membrane preparation methods or modifications will be needed, such as crosslinking, grafting, copolymerization, plasma polymerization, polymer blending or polymer modification, leading to more thermally and chemically stable membranes. For commercialization of new membranes asymmetric and thin-film composite membranes have to be developed.

Another important field that still has to be developed further is the aspect of membrane modules. Until now mainly plate-and-frame modules are used in commercial plants, but for large scale applications in the chemical industry these modules require to much volume (vacuum). Hollow fiber technology, which is under development for gas separation applications now, and spiral-wound module technology (which has recently be developed for pervaporation by MTR), can also provide important advantages for pervaporation.

1.4 Structure of this thesis

This thesis describes research that was aimed at studying two aspects of membrane performance in pervaporation:

1. development of highly selective dense (non-porous) pervaporation membranes for the dehydration of ethanol.
2. understanding the transport mechanism of pervaporation.

Since the development of new membranes is strongly related to understanding the fundamental aspects of the process, like sorption and diffusion of liquids in polymers, these two aspects usually are investigated simultaneously and interactively.

To study the transport mechanism for pervaporation only dense (non-porous) membranes have been investigated. It should be mentioned that in this thesis we always used the term 'homogeneous' membranes for these dense and non-porous membranes. To compare membranes of different thicknesses we generally normalized the fluxes to a thickness of 10 μm (unless stated otherwise), using a proportional relationship between the flux and the reciprocal thickness of the dry membranes. All membranes prepared showed a preferential permeation and a preferential sorption of water from ethanol/water mixtures. Hence, the selectivities of the membranes (pervaporation or equilibrium sorption), always mean the selectivity for water.

In this chapter 1 an introduction was given on membrane filtration in general, and more specific on pervaporation. It is shown that the properties of pervaporation membranes are determined by a great number of factors, which makes a study on transport phenomena of these membranes quite difficult.

In chapter 2 the solution-diffusion model is considered with respect to pervaporation, and it is applied to the separation of ethanol/water mixtures at 25°C using homogeneous poly(vinylalcohol) (PVA) membranes. The influence of sorption and diffusion on the total separation mechanism is investigated.

In chapter 3 more results are presented about pervaporation experiments using homogeneous PVA membranes for the dehydration of ethanol/water mixtures. The permeation results are compared with equilibrium sorption experiments using the same membranes. The influence of the crystallinity of the membranes is investigated by varying the degree of hydrolysis of the PVA or by applying a heat-treatment.

In chapter 4 results are presented about pervaporation experiments using homogeneous poly(acrylonitrile) membranes. These membranes are known to be extremely selective for the dehydration of ethanol/water mixtures. The influence of membrane thickness on flux and selectivity is studied.

In chapter 5 membranes of homogeneous blends of very selective polymers (poly(acrylonitrile) and poly(sulfone)) with hydrophilic polymers are studied, in order to increase the low fluxes of the selective polymer membranes.

In chapter 6 the effects of concentration polarization on pervaporation results are shown, by using numerical examples.

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Chapter 2

Solution-diffusion aspects in the separation of ethanol/water mixtures using homogeneous poly(vinylalcohol) membranes.

J.W.F. Spitzen, E.J.A. Elsinghorst, M.H.V. Mulder, C.A. Smolders

Summary

Transport of liquids and liquid mixtures through homogeneous membranes is described by the solution-diffusion model. From this model the influence of sorption and diffusion on the total transport properties during pervaporation can be deduced. While diffusion is the rate-determining step, separation of a liquid mixture is usually determined by the selective sorption of one of the components into the polymer. The influence of selective diffusion through the membrane can be derived from the sorption selectivity and the pervaporation selectivity.

The preferential sorption model, based on Flory-Huggins thermodynamics, describes total and preferential sorption of a liquid mixture in amorphous polymers in the equilibrium state. The effect of crosslinking and crystallinity of the polymer on the sorption characteristics is described, and demonstrated by some numerical examples.

Experimental sorption and pervaporation results of ethanol/water mixtures using homogeneous poly-(vinylalcohol) (PVA) membranes are presented. For all feed concentrations water is absorbed preferentially and water permeates preferentially. From these results the influence of both sorption and diffusion on the separation mechanism is discussed. Finally the preferential sorption of ethanol/water mixtures in these membranes is predicted by a model. The agreement between the model and the experiments is qualitatively good.

2.1 Introduction

Although a commercial membrane [2.1] is presently available (manufactured by GFT), research on the dehydration of ethanol (or in general on the dehydration of organic solvents) is still continuing. Generally speaking, from a more fundamental point of view it is very interesting to understand why certain polymers show better membrane performance, or which criteria could be important in selecting a polymer for a specific separation problem. Therefore, more information is

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This chapter has been presented in a revised form at the Second International Conference on Pervaporation Processes in the Chemical Industry; San Antonio (USA), March 8-11, 1987 [2.37].

needed about the separation process itself. The model most commonly used to describe the pervaporation process is the *solution-diffusion model.*

This model is generally used to describe transport for membrane processes, where dense (non-porous) membranes are used. Hence, it can be applied to various membrane separation processes, such as reverse osmosis, gas separation and pervaporation. According to this model the selectivity of the separation process is determined by differences in sorption and in diffusion rates of the components in the polymer. Because sorption and diffusion phenomena are mainly determined by the molecular structure of the polymer material, these considerations can give an indication which type of polymers should be used as a membrane material for a specific separation problem. High selectivities for the separation of binary mixtures can be expected when the diffusivities and the solubilities of the components in the membrane differ to a large extent.

In the case of gas separation the polymer generally absorbs only a small amount of both components, and the components will permeate more or less independently from each other. This means that the transport rate for a large part is determined by the diffusivities of the components in the membrane, and the difference in diffusion coefficients then contributes importantly to the overall selectivity. As a result, the choice of a polymer for gas separation problems will strongly be determined by the diffusivities of the components in the polymer material.

In liquid separation processes the absorption of the components in the polymer membrane generally is much higher. As a result, during transport through the membrane coupling phenomena will occur, both in the solution part as well as in the diffusion part. The presence of one component in the membrane will generally increase both the sorption and the diffusion of the other component. As a result the diffusion rates of both components will not differ to a large extent, and the selectivity for permeation will mainly be dominated by the sorption properties of both components. This was confirmed by experimental results [2.2-2.7], from which it was concluded that preferential sorption of a component from a liquid mixture results in preferential permeation of that component during permeation.

Following these considerations, in the case of dehydration of ethanol/water mixtures by pervaporation, a polymer material has to be selected on the basis of differences in sorption capacities for ethanol and water. The polymer should provide high water sorption in comparison with ethanol, which might suggest the selection of hydrophilic polymers. However, the affinity of the polymer towards water must not be to high, because this leads to extensive swelling, resulting in an increased sorption of ethanol. Furthermore, generally ethanol can also form hydrogen bonds with hydrophilic polymers. Hence, a subtile balance between the hydrophilicity of the polymer and swelling must be found; this can be influenced by crosslinking or by increasing the crystallinity.

In the theoretical part of this chapter the solution-diffusion model will be discussed, and the sorption of liquids and liquid mixtures in amorphous, semi-crystalline and crosslinked polymers will be described.

In the experimental part results will be shown on the sorption of ethanol/water mixtures in homogeneous poly(vinylalcohol) (PVA) membranes. These results can be compared with results published earlier about sorption in PVA powder [2.8]. Also pervaporation experiments are performed, from which the influence of diffusion on the separation mechanism can be deduced, by comparing the pervaporation results with the sorption results.

2.2 Theory

In this theoretical part the solution-diffusion model will be presented, describing transport through homogeneous membranes. By this model the influence of sorption and of diffusion on the total transport rate and on the separation characteristics during pervaporation can be evaluated. The sorption part is assumed to determine the overall selectivity of the pervaporation process [2.9]. Because the sorption of liquids in polymers can be influenced easily by crosslinking or by changing the crystallinity of the polymer, these factors also should have a strong influence on the overall pervaporation characteristics. In this paragraph the influence of crosslinking and crystallinity on the total and the preferential sorption is discussed and illustrated by some numerical examples.

2.2.1 The solution-diffusion model

Transport through dense (non-porous) homogeneous membranes is usually described by a solution-diffusion model [2.10-2.12]. According to this model each component of a mixture dissolves into the membrane and diffuses through the membrane due to a driving force. The driving force generally is the gradient in the chemical potential across the membrane. Hence, the flux of a component i is given by:

$$J_i = - D_i.c_i^m.d(\mu_i^m/RT)/dx \qquad (1)$$

For isothermal conditions the chemical potential is given by:

$$d(\mu_i^m/RT)_T = d(\ln a_i^m) + (V_i/RT).dP \qquad (2)$$

For pervaporation the pressure gradient across the membrane can be neglected in comparison with the activity gradient, as can easily be shown by simple calculations. Equation (1) can be rewritten as:

$$J_i = - D_i . c_i^m . d(\ln a_i^m)/dx \qquad (3)$$

From this equation it can be seen that the two important factors determining the transport properties of a membrane are the diffusion coefficient and the concentration (or activity) of the components in the membrane. Hence, the separation of a liquid mixture is caused by differences in diffusion rates and by differences in sorption. When selecting a polymer for a certain separation problem both sorption and diffusion should be considered.

Because sorption and diffusion take place at the same time, it is impossible to investigate experimentally both processes separately. Because the solution-diffusion model assumes that the sorption process is fast compared to diffusion through the membrane during permeation, according to this model equilibrium sorption experiments can be used to obtain the concentration of the components in the membrane at the feed side. From the pervaporation results and the equilibrium sorption results information can be deduced about the diffusion of the components through the membrane.

The pervaporation selectivity α^P is calculated from the liquid composition of the feed (f) and the permeate (p):

$$\alpha^P_{i/j} = (c_i^p/c_j^p)/(c_i^f/c_j^f) \qquad (\alpha^P_{i/j} > 1) \qquad (4)$$

In the same way an equilibrium sorption selectivity α^S can be defined as a function of the liquid composition of the feed (f) and the liquid composition in the swollen membrane (m):

$$\alpha^s_{i/j} = (c_i^m/c_j^m)/(c_i^f/c_j^f) \qquad (5)$$

Because the pervaporation selectivity is only determined by differences in sorption and diffusion, the difference between α^P and α^S must be caused by differences in diffusion (a similar approach was used by Bell [2.13] and Larchet et al [2.3]). Hence, a diffusion selectivity can be defined as the ratio between the pervaporation selectivity and the equilibrium sorption selectivity:

$$\alpha^d = \alpha^p / \alpha^s \qquad (6)$$

Combination of equations (4)-(6) results in :

$$\alpha^d = (c_i^p/c_j^p)/(c_i^m/c_j^m) = (J_i/J_j)/(c_i^m/c_j^m) \qquad (7)$$

By substituting $a_i=\gamma_i.c_i$ and for constant activity coefficients γ_i ($d\gamma_i/dx=0$) equation (3) can be converted into:

$$J_i = - D_i.d\, c_i^m/dx \qquad (8)$$

In case of constant diffusion coefficients (independent of concentration) and zero concentration of the components at the permeate side of the membrane the ratio of the component fluxes can be obtained by integration of equation (8):

$$J_i/J_j = (D_i.c_i^m)/(D_j.c_j^m) \qquad (9)$$

Substitution of equation (9) in (7) gives:

$$\alpha^d = D_i/D_j \qquad (10)$$

Equation (10) still holds for concentration dependent diffusion coefficients, if D_i and D_j are considered as the mean or effective diffusion coefficients.

It should be kept in mind that equation (10) is derived using the following assumptions:

- isothermal conditions of the process. Because due to the phase transition during permeation a temperature gradient will be present across the membrane, also an entropy effect can contribute to the overall driving force.
- sorption during pervaporation is an equilibrium process.
- constant activity coefficients ($d\gamma_i/dx=(d\gamma_i/dc_i).(dc_i/dx)=0$). For some liquid mixtures activity coefficients strongly depend on the composition of the mixture ($d\gamma_i/dc_i\neq0$).
- zero concentration of the components at the permeate side of the membrane.

Hence, the approach given above to deduce information about diffusivities, must be considered qualitatively as a first approach only to this problem.

It should be kept in mind that sorption experiments are equilibrium experiments, whereas pervaporation experiments are non-equilibrium experiments. Mulder et al [2.14] performed equilibrium sorption experiments with water and ethanol separately, and with an ethanol/water mixture in homogeneous CA membranes. Using the same membranes, concentration profiles for the pure components as well as for the mixture were measured during pervaporation. In table 2.1 the equilibrium sorption results are compared with the concentrations in the membrane at the feed side during pervaporation. From this table it can be seen that only in the case of pure water the equilibrium sorption value is equal to the sorption value during pervaporation. In all other cases the sorption during pervaporation is lower than the equilibrium sorption values, which is an indication for the fact that sorption of the components is not infinitely fast compared to diffusion through the membrane. This phenomenon of lower total sorption in the case of permeation compared to equilibrium sorption has also been reported for some other systems [2.15-2.16]. If from the sorption results of table 2.1 the binary liquid composition in the membrane is calculated, the results are quite the same for both equilibrium sorption and sorption during pervaporation. So, although the total sorption in both cases is not the same, the preferential sorption is comparable. However, it is obvious that this can not be generalized to apply to other systems likewise; for such a conclusion more information is needed.

Table 2.1: Comparison between equilibrium sorption data and sorption data during pervaporation, for an ethanol/water mixture (65 w% ethanol) in homogeneous CA membranes, at 20°C [2.14]; Q_i = grams of absorbed liquid/gram dry polymer.

		equilibrium sorption			*sorption during pervaporation* (at the feed side in the membrane)		
	component	w% liquid	Q_i (g/g)	w% ethanol (liquid fraction)	w% liquid	Q_i (g/g)	w% ethanol (liquid fraction)
pure liquids:	water	12.5	0.143		12.5	0.143	
	ethanol	17.7	0.215		10.9	0.122	
liquid mixture	water	14.7	0.197		10.0	0.120	
(65 w% ethanol,	ethanol	10.6	0.142		6.9	0.083	
35 w% water)	total	25.3	0.339	40.9	16.9	0.203	40.0

Hence, the pervaporation characteristics of dense, homogeneous membranes are determined by the sorption and diffusion phenomena of liquids in the polymer. While sorption and diffusion properties are mainly determined by the choice of the polymer, both sorption [2.17-2.20] and diffusion [2.21-2.24] (and thus permeation) of components can strongly be influenced by the crystallinity (of semi-crystalline polymers) or crosslinking. The influence of crystallinity and crosslinking on the sorption of low molecular weight components in polymers will be described mathematically in this section. Experimental results concerning the influence of crystallinity on the pervaporation characteristics of homogeneous PVA membranes will be presented in the next chapter.

2.2.2 Sorption of liquids in amorphous polymers

When a liquid is brought into contact with a dry polymer, it will be absorbed into the polymer as a result of the activity gradient over the contact surface. This swelling is due to the possible interactions between the liquid molecules and the polymer. After a certain period of time an equilibrium is reached: the activity of the liquid in the polymer is equal to the activity of the bulk liquid. If a *pure liquid* is considered, the sorption process is characterized by the amount of liquid absorbed: *total sorption.* If the polymer is brought into contact with a *liquid mixture,* both components of the liquid tend to penetrate the polymer. Since usually the interactions between the individual components and the polymer are different, the liquids will not be absorbed to the same extent and *preferential sorption* occurs. Hence, sorption of a liquid mixture in a polymer is characterized by both *total sorption* and *preferential sorption.*

The sorption process is considered as ideal, if the sorption of a component i from a mixture is proportional to the concentration of this component x_i in the feed mixture: $c_i^m=x_i.c_i^\circ$, where c_i° is the sorption of the pure component i in the polymer. As a result the total sorption of the mixture is a linear function of the feed composition of the liquid mixture; the sorption selectivity (as defined by equation (5)) for such a system is independent of the liquid composition. Ideal sorption can be expected for systems where the interactions between the liquid components are weak, and the total sorption is very small due to a weak interaction between the polymer and penetrants, e.g. in case of sorption of gases in polymers. Many authors have assumed that ideal sorption takes place during pervaporation [2.10,2.25-2.28]. In pervaporation however, the interactions between the polymer and the penetrants (liquids) are stronger, generally resulting in higher sorption values of the components in the polymer. In that case the sorption of a component is not only dependent on its own concentration in the feed, but will also be influenced by the presence (absorption) of the other component. Hence, experimental deviations from ideal sorption are usually found for sorption of liquid mixtures in polymers [2.2,2.4,2.14,2.29-2.30], although exceptions are possible [2.31].

Total sorption

Relations describing equilibrium sorption of low molecular weight components in polymers are usually derived from Flory-Huggins thermodynamics [2.17].

In the case of sorption of a *pure liquid* i in a polymer the following equation can be derived for the binary system:

$$\Delta\mu_i/(RT) = \ln a_i = \ln(1 - \phi_p) + \phi_p(1 - 1/n_i) + \chi_{ip}\phi_p^2 = 0 \qquad (11)$$

(amorphous polymer; one liquid component)

The swelling of the polymer, denoted by $1\text{-}\phi_p$ (where ϕ_p is the volume fraction of polymer) can be calculated from this equation when the interaction parameter χ_{ip} is known. This binary interaction parameter is characterizing the difference in energy of a penetrant molecule absorbed in a pure (amorphous) polymer compared with the energy of a molecule in the pure penetrant. Although in the original Flory theory the interaction parameter is considered as an enthalpy parameter, from a physical point of view it is more convenient to consider it as a free enthalpy parameter, taking into account all the non-ideality of the system, including both the non-ideal enthalpy and entropy of mixing. In polymer solutions χ values are less than 0.5; in swollen polymers χ is usually higher than 0.5, and generally increases when the affinity between penetrant and polymer decreases. Whereas the enthalpy contribution of the interaction parameter usually can be predicted by the solubility parameter theory [2.32-2.34], the difficulty in predicting interaction parameters originates from the contribution of the entropy term, which cannot be estimated from theory yet.

Preferential sorption

When a polymer is immersed in a *binary liquid mixture*, two parameters are needed to characterize the ternary system: the *total sorption* (denoted by $1\text{-}\phi_p$) and the *preferential sorption*. The preferential sorption is a measure for the difference of the liquid compositions in the binary liquid feed and in the binary liquid fraction in the swollen polymer (ternary system).

For the separation of liquid mixtures by pervaporation this preferential sorption is a very important parameter [2.9]. The preferential sorption in the equilibrium state can also be described by relations derived from Flory-Huggins thermodynamics. The preferential sorption can be characterized by the sorption selectivity α^S, as defined by equation (5). When the volume fractions of the liquids 1 and 2 in the ternary system are denoted by ϕ_1 and ϕ_2 respectively ($\phi_1+\phi_2+\phi_p=1$) and the volume fractions in the binary liquid feed by v_1 and v_2, the following equation can be derived for the preferential sorption [2.2]:

$$\ln \alpha^s = \ln\left(\frac{\phi_1}{\phi_2}\Big/\frac{v_1}{v_2}\right) =$$

$$= \left(\frac{1}{m}-1\right) \ln\left(\frac{\phi_2}{v_2}\right) - \chi_{12}\Big((v_1 - v_2) - (\phi_1 - \phi_2)\Big) - \phi_3\left(\chi_{13} - \frac{1}{m}\chi_{23}\right) \qquad (12)$$

(amorphous polymer; two liquid components)

In this equation three constant (concentration independent) interaction parameters are used, characterizing the interaction energy of liquid 1/liquid 2 (χ_{12}), liquid 1/polymer (χ_{13}) and liquid 2/ polymer (χ_{23}). For calculating the preferential sorption (or ϕ_1 and ϕ_2) these three interaction parameters and the total sorption (or ϕ_p=ϕ_3) must be known.

In the most simple case the interaction parameters are constant and can be obtained from swelling data of the polymer in the pure liquids using equation (11) (in case of χ_{13} and χ_{23}), or from literature. But generally the interaction parameters have to be chosen to be concentration dependent, in order to obtain good quantitative agreement between experiments and the theoretical model [2.2].

2.2.3 Sorption of liquids in crosslinked and in semi-crystalline polymers

The equations used above were derived for sorption of liquids in *amorphous* polymers. But many polymers are semi-crystalline or can be crosslinked. Crosslinking and crystallinity both can influence the total and preferential sorption of liquids in polymers.

Because sorption is an important factor in the transport mechanism of pervaporation, also flux and pervaporation selectivity of a membrane will be influenced by crystallinity and crosslinking. Crosslinking restricts swelling of the polymer and therefore the concentration of the liquid in the polymer is decreased. Because in most cases the diffusion coefficient is concentration dependent, also the diffusion coefficient of the components in the membrane will decrease. In the case of crystallinity, transport rates of the components will also decrease: the crystallites can be considered as physical crosslinks, resulting in the same effects as chemical crosslinking. Furthermore, crystallites are impermeable to penetrants, leading to hindered diffusion (tortuosity effect); this also results in smaller fluxes.

Total sorption

Following the literature, the effect of crosslinking and crystallinity on the sorption of low molecular weight components in polymers can be taken into account.

A method that is followed by many authors, is to use equation (11) (sorption in amorphous polymers), and to consider χ_{ip} in that equation as an overall interaction parameter for the crosslinked or semi-crystalline polymer; the interaction parameter calculated in this way can be considered as an empirical fit-parameter. This method can be used when no quantitative information is present about the crosslinking density or the crystallinity of the polymer of interest.

Following a more fundamental approach, the *total sorption* (characterized by $1-\phi_p$) of a pure liquid i in a crosslinked or semi-crystalline polymer can be described by the following equations (from [2.17] and [2.35] respectively):

$$\ln\left(1-\phi_p\right)+\phi_p\left(1-\frac{1}{n_i}\right)+\chi_{ip}\phi_p{}^2+V_i\frac{\rho_p}{M_c}\left(\phi_p{}^{1/3}-2\phi_p/f\right)=0 \qquad (13)$$

(crosslinked polymer; one liquid component)

and:

$$\ln\left(1-\phi_p\right)+\phi_p\left(1-\frac{1}{n_i}\right)+\chi_{ip}\phi_p{}^2+V_i\frac{\rho_p}{M_u}\left(\frac{\Delta H_f/R\left(\frac{1}{T}-\frac{1}{T_m'}\right)}{\left(\frac{3}{2\lambda\phi_p}-1\right)}\right)=0 \qquad (14)$$

(semi-crystalline polymer; one liquid component)

In these equations M_c (molecular weight between two crosslinks) and λ (fraction of non-crystalline polymer that is elastically effective) represent the influence of crosslinking or crystallinity respectively.

As an example, the effect of crosslinking on the total sorption will be given here for two pure liquids 1 and 2. The volume fraction of polymer ϕ_p is calculated using equation (13). In order to calculate χ_{1p} and χ_{2p} from the sorption of the pure liquids 1 and 2 in the amorphous polymer using equation (11), volume fractions $\phi_{p1}=0.60$ and $\phi_{p2}=0.80$ have been used. The molar volumes V_i of the liquid components 1 and 2, and of the polymer (component 3) are 20 cm^3/mole, 50 cm^3/mole, and 10^6 cm^3/mole respectively. The density of the polymer is 1.3 g/cm^3, the crosslinks are tetra-functional (f=4). The results are given in figure 2.1; the figure indeed shows that, when decreasing the molecular weight between crosslinks (higher degree of crosslinking), the volume fraction of polymer increases strongly (i.e. the swelling decreases).

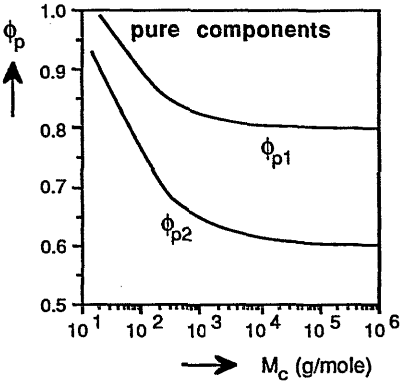

Figure 2.1: Swelling of a crosslinked polymer in pure liquids 1 and 2, as a function of the crosslinking density (M_c= molecular weight between crosslinks); for numerical data see text.

Preferential sorption

Crosslinking and crystallinity will also influence the preferential sorption of a liquid mixture in a polymer. The *preferential sorption* can still be calculated using equation (12); this equation does not show any direct effects of crosslinking and/or crystallinity parameters. Two situations can be distinguished:

- the prediction of the sorption selectivity of a crosslinked or semi-crystalline polymer on basis of sorption data of the same amorphous polymer; or
- the description of an experimentally determined sorption selectivity of the crosslinked or semi-crystalline polymer, treating it either as an amorphous, as a crosslinked or as a semi-crystalline polymer.

If equation (12) is used to *predict* the preferential sorption, and if it is assumed that the interaction parameters χ_{13} and χ_{23} for the penetrants and the polymer are not changed by introduction of crosslinks or crystallinity in the polymer, the total sorption of the pure components as well as that of the liquid mixture in the polymer will be smaller compared to sorption in an amorphous polymer (see equations (13) and (14) compared to (11)). Due to this decrease in ϕ_p the preferential sorption will change too. Hence, in this case the solution of equation (12) is influenced due to a change in ϕ_p.

The effect of the degree of crosslinking on the preferential sorption is demonstrated in figure 2.2. For a 50/50 (vol%) feed the sorption selectivity α^S is given as a function of M_c, as calculated by equation (12), using the same data as for computing figure 2.1. The interaction parameter for the liquid mixture was taken as χ_{12}=1.0. Figure 2.2 shows that upon increasing the degree of crosslinking the sorption selectivity increases. It is clear that the sorption selectivity should increase strongly when the crosslinking density reaches the level, at which the molar volume between the crosslinks V_{pc} is of the same order of magnitude as the molar volume of the 'largest' component V_2, i.e. $V_{pc}=M_c/\rho_p \approx V_2$, or $M_c \approx V_2.\rho_p$. For the parameters chosen in this example the 'critical' molecular weight between crosslinks is $M_c \approx 50*1.3=65$ g/mole, which is in agreement with the strong increase of the sorption selectivity in figure 2.2. It should be recognized that in many polymers the molecular weight of a monomeric unit is larger than this value of 65 g/mole, which means that in practical cases, for the numerical data used in this example, the effect of crosslinking at more realistic crosslinking densities is only very small.

It can be shown by calculations that the effect of crosslinking on the preferential sorption increases when the difference in solubilities of the two pure components is greater.

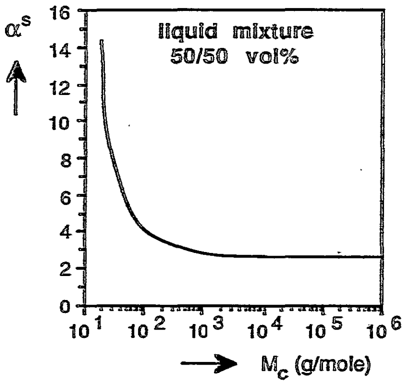

Figure 2.2: Preferential sorption of a liquid mixture of components 1 and 2 in a crosslinked polymer, as a function of the crosslinking density (M_c= molecular weight between crosslinks); for numerical data see text.

On the other hand, equation (12) can also be used to *describe* the preferential sorption in a polymer for which the preferential sorption is measured experimentally. It can be investigated whether the prediction of the sorption selectivity is improved when the polymer is treated either as amorphous, semi-crystalline or crosslinked. In that case the interaction parameters χ_{13} and χ_{23} to be used in equation (12) must be different when calculating these from the experimental ϕ_3 by equation (11) for amorphous polymers, by equation (13) for crosslinked or by equation (14) for semi-crystalline polymers. Hence, in this case the preferential sorption is influenced by changing the interaction parameters χ_{13} and χ_{23}, while ϕ_3 is given by experiment.

2.3 Experimental

2.3.1 Materials

Poly(vinylalcohol) (M_w=115,000 Dalton; 100% hydrolyzed) was obtained from Janssen Chimica. Dimethylsulfoxide (DMSO) (reagent grade) and ethanol (analytical grade) were used without further purification; water was ultrafiltrated before use.

2.3.2 Membrane preparation

Casting solutions were prepared by dissolving PVA in DMSO (10 or 20 w%). Upon heating to about 55°C a clear solution was obtained. Homogeneous membranes were prepared by casting the solution on a glass or perspex plate. The solvent was removed by evaporation in a nitrogen atmosphere at room temperature. The membranes were used without post-treatments.

2.3.3 Sorption experiments

Strips of PVA membranes (thickness of about 50 μm, dry weight of about 0.4 g.) were dried in vacuo until no significant weight decrease was observed anymore. The strips were immersed in conical flasks containing water, ethanol or a mixture of both. The flasks were placed in a thermostated bath at 25°C. The weight of the membranes was measured until no significant weight increase could be observed. After equilibrium was reached the membranes were removed, blotted between tissue papers and put into a closed tube. The sorbed liquid was distilled out of the membrane, by a method described by Mulder et al [2.2]. From the wet weight (after equilibrium sorption) and dry weight (after distillation) of the membranes and the composition of the absorbed liquid, the total sorption and the preferential sorption were calculated. All experiments were performed in triplo, and the results were averaged. The total sorption is represented by Q: grams of absorbed liquid per gram dry polymer. The preferential sorption is represented by the equilibrium sorption selectivity α^s, which is calculated from the liquid composition of the feed (f) and the composition of the absorbed liquid in the membrane (m), according to equation (5) (taking i=water and j=ethanol). The composition of the liquids was determined by gas chromatography.

2.3.4 Pervaporation experiments

The pervaporation experiments were performed employing three stainless steel pervaporation cells. The effective membrane area in each cell is 79 cm^2. From the feed tank, which is kept at a constant temperature of 25°C, the feed is circulated through the three cells. The pressure at the downstream side was kept below 500 Pa by a vacuum pump. The permeate was collected in cold traps, which were cooled by liquid nitrogen. Fluxes were determined every hour during eight hours by determination of the weight increase of the cold traps. During the night pervaporation continued, the permeate then being collected in a large condenser (cooled by a cryostat at -30°C). Experiments for each run were performed for at least 2 days. A schematic representation of the experimental setup is given in figure 2.3. The pervaporation properties are characterized by the flux J and the pervaporation selectivity α^P.

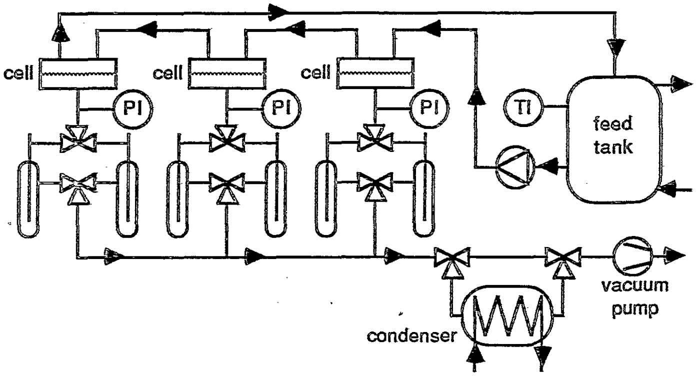

Figure 2.3: Schematic representation of the experimental pervaporation apparatus.

The fluxes of the different membranes were normalized to a membrane thickness of 10 µm, assuming a proportionality between the flux J and the reciprocal membrane thickness 1/d: J_n=J.d/10 (kg/m^{2}h).

The pervaporation selectivity α^P was calculated from the liquid composition of the feed (f) and the permeate (p) according to equation (4) (taking i=water and j=ethanol). α^P is assumed to be independent of membrane thickness within the range of thicknesses used (dry thickness between 10 and 15 µm). The composition of the liquids was determined by gas chromatography.

2.4 Results and discussion

2.4.1 Sorption

The results of the sorption experiments of ethanol/water mixtures in the PVA membranes are given in the figures 2.4-2.5.

In figure 2.4 the total sorption Q is given as a function of the feed composition. It shows that the swelling of the membranes increases with increasing water content of the feed. Using pure water, the liquid uptake is about twice of the original polymer weight, whereas for pure ethanol the liquid uptake is only a few percent.

Figure 2.4 also includes results from literature [2.8], where PVA *powder* was used instead of homogeneous *membranes*, as in our case. Although the trend for both systems is the same, the powder generally absorbs more liquid than the membrane. Only at high water concentrations in the feed the sorption of the membrane was higher. The discrepancy between the results might be due to differences in crystallinity between the PVA samples. Unfortunately no quantitative considerations can be given, because information on the crystallinity of both samples was not available.

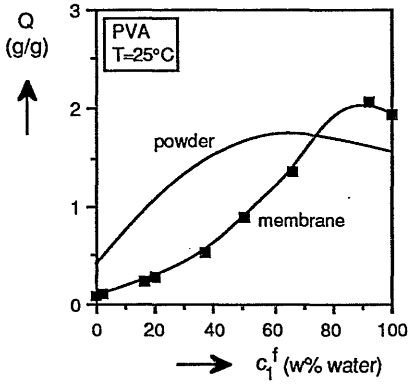

Figure 2.4: Total sorption Q (grams of absorbed liquid/gram dry polymer) for PVA powder (from [2.8]) and for homogeneous PVA membranes (■), as a function of the water content in ethanol/water mixtures.

Another uncertainty is the difference between the experimental methods used for the determination of the sorption properties. Whereas we used vacuum distillation to examine the sorption of the swollen membranes, Neel et al [2.8] used a depletion method to calculate the concentrations inside the PVA powder. From this reference it could not be concluded how exactly the total sorption was determined. It should be mentioned that a depletion method is an indirect method, which can be very sensitive to small experimental errors.

In figure 2.5a the composition of the absorbed liquid in the polymer is plotted as a function of the feed concentration, both for the powder (data taken from [2.8]) and for the homogeneous membranes. In both cases water is absorbed preferentially over the whole composition range, but the preferential sorption for the membrane is much higher than for the powder. This can be explained from the lower total sorption in the membranes (as can be deduced from equation (12)): the higher the polymer fraction in a swollen system, the greater the preferential sorption for the smaller component (water).

In figure 2.5b also the preferential sorption results are shown, in which the sorption selectivity is given as a function of the feed concentration. For all feed concentrations water is absorbed pre-ferentially. At very low water concentrations a rather high sorption selectivity was found (α^s=72, for 0.2 w% water in the feed), but with increasing water concentration this value de-creased rapidly to a value of about 3. The sorption selectivity for the powder is not plotted in figure 2.5b, because this value is very low, being between α^s=1.2 and α^s=1.5 over the complete feed composition range.

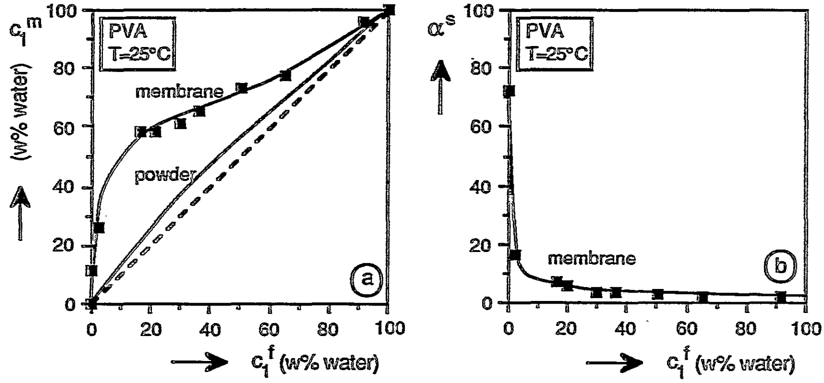

Figure 2.5: Composition of the absorbed liquid in the swollen polymer c_1^m (a) and sorption selectivity α^S (b), for PVA powder (from [2.8]) and for homogeneous PVA membranes (■), as a function of the water content in ethanol/water mixtures.

Prediction of preferential sorption

The preferential sorption of ethanol/water mixtures in the PVA membranes can be predicted from equation (12), using constant interaction parameters. However, generally a better agreement between experiments and the model is found if concentration dependent interaction parameters are used. Because for binary liquid mixtures the concentration dependence of χ_{12} (g_{12}) can be deduced from literature sources, a modified form of equation (12) is used, in which only χ_{13} and χ_{23} are kept constant [2.2]:

$$\ln \alpha^s = \ln\left(\frac{\phi_1}{\phi_2} \bigg/ \frac{v_1}{v_2}\right) =$$

$$= \left(\frac{1}{m} - 1\right) \ln\left(\frac{\phi_2}{v_2}\right) - g_{12}(v_2)(v_1 - v_2) + g_{12}(u_2)(\phi_1 - \phi_2) - \phi_3\left(\chi_{13} - \frac{1}{m}\chi_{23}\right) +$$

$$+ u_1 \phi_2 \frac{dg_{12}(u_2)}{du_2} - v_1 v_2 \frac{dg_{12}(v_2)}{dv_2} \qquad (15)$$

where $u_2 = \phi_2/(\phi_1 + \phi_2)$.

The concentration dependent binary interaction parameter for ethanol/water mixtures (taking 1=water and 2=ethanol) g_{12} at 25°C was calculated from excess free energy of mixing data [2.36 The data were interpolated and the dependence of g_{12} on the volume fraction of ethanol was fitted to a third grade polynomial function:

$$g_{12}(x) = 0.7879 + 0.2026\,x + 0.6080\,x^2 - 0.2101\,x^3 \qquad (T=25°C) \qquad (16)$$

Because it is assumed that g_{12} is only dependent on the liquid composition, this equation is used both for the liquid feed and for the liquid in the swollen ternary system; so equation (16) is used both when $x=v_2$ and when $x=u_2$.

The interaction parameters χ_{13} and χ_{23} are assumed to be constant, and are calculated from the sorption of the pure components in the polymer. From the experimental results weight fractions are transformed into volume fractions, assuming additivity of molar volumes. In this case it is assumed that PVA acts as an amorphous polymer, so equation (11) is used to calculate χ_{13} and χ_{23}. Because a high molecular weight PVA was used, the factor $1/n_i = V_i/V_p$ has been neglected. The final parameters obtained are given in table 2.2.

Table 2.2: Parameters used to predict preferential sorption of ethanol/water mixtures in homogeneous PVA membranes, at 25°C.

property	index i	water 1	ethanol 2	PVA-115-100 3
MW	(Dalton)	18.02	46.07	115,000
ρ_i	(g/cm^3)	0.99708	0.78506	1.3
V_i	(cm^3/mole)	18.073	58.683	89,000
swelling: Q_i	(g/g dry polymer)	1.9317	0.0814	-
ϕ_p	(cm^3/cm^3)	0.284	0.884	-
χ_{i3}	(-)	0.62	1.63	-

To predict the preferential sorption by equation (15) one composition parameter should be known. For practical reasons mostly ϕ_3 is used. This means that ϕ_3 should be determined experimentally as a function of the feed concentration:

$$\phi_3 = \phi_{3,\ \text{from experiment}} \qquad (17a)$$

If no experimental data on sorption of the mixture are available, the total sorption can be estimated from swelling data of the pure components. As a first approximation it can be assumed that the total sorption in the ternary system is a linear function of the composition of the feed mixture, according to:

$$\phi_3 = v_1 \phi_3(v_2{=}0) + v_2 \phi_3(v_1{=}0) \qquad (17b)$$

Another approach is to define an 'average' interaction parameter χ_{m3} for the liquid mixture and the polymer, which is linearly dependent on the composition of the feed mixture, according to:

$$\chi_{m3} = v_1 \chi_{13}(v_2{=}0) + v_2 \chi_{23}(v_1{=}0) \qquad (17c)$$

Substitution of χ_{m3} in equation (11) leads to ϕ_3.

The composition of the liquid in the swollen PVA was calculated by using equation (15), taking experimental total sorption values (17a), and predicted total sorption values from equations (17b) and (17c). The predicted results and the experimental data obtained for the preferential sorption (of water) are given in figure 2.6. From this figure it can be seen that the best fit is obtained for the case in which the experimental ϕ_3 values are used. The agreement between experimental and predicted liquid composition in the membrane is qualitatively reasonable. If also the total swelling has to be predicted from the swelling values in the pure components by equation (17b) or (17c), the agreement is worse. These equations generally predict a higher preferential sorption at low water content of the feed.

In conclusion, a reasonable good agreement can be found between the model and the experiments, using constant interaction parameters (χ_{i3}), and using the experimental total sorption values (ϕ_3).

2.4.2 Pervaporation

The pervaporation results using the PVA membranes are shown in figure 2.7.

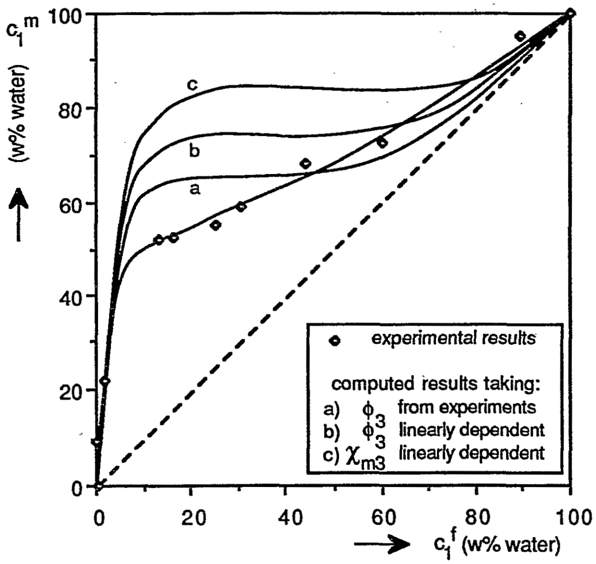

Figure 2.6: Experimental and predicted values of the composition of the liquid in homogeneous PVA membranes, as a function of the water content in ethanol/water mixtures.

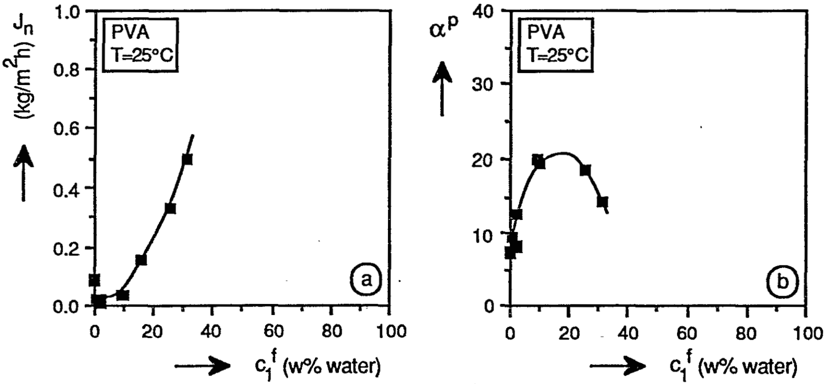

Figure 2.7: Normalized pervaporation flux through homogeneous PVA membranes J_n (a) and pervaporation selectivity α^P (b), as a function of the water content in ethanol/water feed mixtures. Membrane thickness: 10-15 μm.

In figure 2.7a the flux is given as a function of the feed concentration. At low water concentration small fluxes were measured, due to the poor swelling of the membrane. For increasing water concentration in the feed the flux increases rapidly. At concentrations higher than 31 w% water in the feed the swelling of the membrane became so high that due to loss of mechanical strength no pervaporation experiments could be performed anymore. The pervaporation selectivity is given in figure 2.7b. For increasing water concentration the selectivity first increases, but then decreases again. The decrease in pervaporation selectivity is mainly due to the low sorption selectivity at these higher water concentrations.

2.4.3 Sorption versus pervaporation

In figure 2.8 the ratio of the pervaporation selectivity and the equilibrium sorption selectivity is given as a function of the feed concentration. This ratio is called the diffusion selectivity α^d, as defined in equation (7). The diffusion selectivity is equivalent to the ratio of the effective (or mean) diffusion coefficients of water and ethanol (see equation (10)). Interpolation between feed concentrations was used to calculate pervaporation selectivities and sorption selectivities at the same concentration.

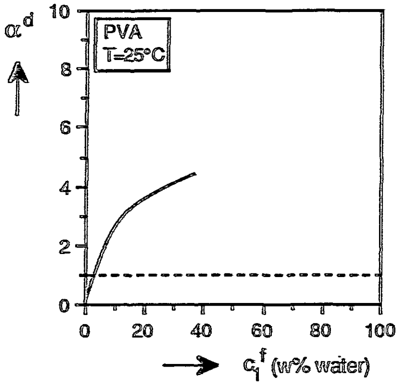

Figure 2.8: Diffusion selectivity α^d for homogeneous PVA membranes, as a function of the water content in ethanol/water feed mixtures (calculated from interpolated values of the equilibrium sorption selectivity and the pervaporation selectivity).

From figure 2.8 it can be seen that the diffusion selectivity increases with increasing water content in the feed. This is probably due to a stronger increase of the diffusion rate of water compared to ethanol, because the membrane mainly absorbs water. At low water content (< 5 w% water) in the ethanol/water mixtures the diffusion selectivity is smaller than the sorption selectivity (actually, the diffusion selectivity is lower than 1), which means that at low water concentrations the preferential permeation of water is mainly determined by the preferential sorption of water from the mixtures; at higher water concentrations the preferential permeation of water is more strongly influenced by the selective diffusion of water. It should be realized that the diffusion selectivity has been derived from equilibrium sorption results in combination with steady-state pervaporation results. If during pervaporation no thermodynamic equilibrium takes place at the feed-membrane interface, the diffusion selectivity, as considered here, has no sound basis.

2.5 Conclusions

In the theoretical part it is shown that, if it can be assumed that preferential sorption during pervaporation is comparable to preferential equilibrium sorption, information about the diffusivities during pervaporation can be obtained by comparing the sorption results and the pervaporation results. By a numerical example it is shown that the preferential sorption of a liquid mixture in a polymer can be influenced by crosslinking. At increasing degree of crosslinking the preferential sorption increases, due to the decrease of the total sorption. The effect of crosslinking on the sorption selectivity is strongly dependent on the molar volumes of the components. If the molecular weight between crosslinks is of the same order of magnitude or smaller than $M_c \approx V_2 \cdot \rho_p$ (V_2= molar volume of the largest component), the sorption selectivity increases strongly.

In the experimental part it is shown that water is preferentially absorbed in homogeneous PVA membranes, for all ethanol/water compositions. At decreasing water concentrations in the feed the sorption selectivity increases strongly. Water also permeates preferentially through these homogeneous PVA membranes, for all ethanol/water mixtures measured. By comparing the equilibrium sorption selectivity and the pervaporation selectivity, it is concluded that diffusion also affects the separation mechanism.

2.6 List of symbols

a_i = activity of component i in the liquid (feed, permeate, membrane) (-)
c_i = weight fraction of component i in the liquid (feed, permeate, membrane) (g/g)
d = membrane thickness (μm)
D_i = diffusion coefficient of component i in the membrane (m^2/h)
f = functionality of the crosslinks (-)
g_{ij} = concentration dependent interaction parameter for components i and j (-)
ΔH_f = heat of fusion of the polymer (J/mole)
J = total pervaporation flux (kg/m^2h)
J_i = pervaporation flux of component i (kg/m^2h)
J_n = total pervaporation flux, normalized to 10 μm membrane thickness (kg/m^2h)
m = ratio of molar volumes of component 2 and component 1: $m= V_2/V_1$ (-)
M_c = molecular weight between two crosslinks (Dalton)
M_u = molecular weight of the monomeric unit of the polymer (Dalton)
M_w = weight average molecular weight of the polymer (Dalton)

n_i = ratio of molar volumes of the polymer and component i: $n_i = V_3/V_i$ (-)
Q = total sorption in the polymer: grams of absorbed liquid/gram dry polymer (g/g)
R = gas constant (J/mole.K)
T = temperature (°C, K)
T_m' = melting temperature of the crystallites in the polymer (K)
u_i = volume fraction of component i in the binary liquid in the swollen polymer (cm^3/cm^3)
v_i = volume fraction of component i in the liquid feed (cm^3/cm^3)
V_i = molar volume of component i (cm^3/mole)
x_i = mole fraction of component i (mole/mole)

α = selectivity (equilibrium sorption, pervaporation, diffusion) (-)
χ_{ij} = concentration independent interaction parameter for components i and j (-)
χ_{m3} = concentration independent interaction parameter for a liquid mixture and a polymer (-)
ϕ_i = volume fraction of component i in the ternary system (cm^3/cm^3)
λ = fraction of non-crystalline polymer that is elastically effective (cm^3/cm^3)
μ = chemical potential (J/mole)
ρ = density (g/cm^3)

<u>subscripts</u>
1 = preferentially permeating component
2 = less permeable component
3 = polymer
p = polymer

<u>superscripts</u>
d = diffusion
f = feed
m = membrane
p = permeate, pervaporation
s = sorption
° = related to the pure component

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Chapter 3

Pervaporation of ethanol/water mixtures using homogeneous poly(vinylalcohol) membranes.

J.W.F. Spitzen, M.H.V. Mulder, C.A. Smolders

Summary

Ethanol/water mixtures were dehydrated by pervaporation using homogeneous poly(vinylalcohol) (PVA) membranes. The pervaporation flux and selectivity were determined at 25°C as a function of the feed composition, using four types of PVA with different degrees of hydrolysis. With the same membranes equilibrium sorption experiments were performed, from which information about the separation mechanism was obtained. In all cases both pervaporation flux and total swelling of the membranes increased with increasing water content in the ethanol/water mixtures. At high ethanol concentrations the fluxes were extremely small (except for 88% hydrolyzed PVA), due to the fact that the solubility of pure ethanol in these membranes is extremely small. Ethanol was only absorbed in the membranes in the presence of water.

Homogeneous PVA membranes with a high degree of hydrolysis were also tested at 90 w% ethanol and 70°C. The flux and selectivity were determined as a function of membrane thickness, for different preparation methods. Whereas the fluxes of the membranes were rather reproducible, the selectivities varied to a large extent. The influence of crosslinking of the membranes with maleic acid on the pervaporation properties was investigated.

All PVA membranes prepared were semi-crystalline. The crystallinity of the membranes was dependent on the degree of hydrolysis of the PVA used, and was increased by a heat-treatment. The presence of crystallites determines to a large extent the sorption and pervaporation properties of PVA membranes.

3.1 Introduction

Pervaporation is a membrane separation technique, that can be used to separate liquid mixtures. In the beginning of the research on pervaporation in the early sixties [3.1-3.5] mostly mixtures of organic liquids were investigated, but both the separation efficiency and the permeability were too low to compete with conventional liquid separation techniques, such as distillation and extraction. Furthermore, in that time the energy prices were rather low, so there was little need for alternative, less energy consuming separation techniques. The dehydration of water/organic liquid mixtures seemed to be more promising, in which case generally hydrophilic polymers have to be used as a membrane material. Especially the separation of ethanol/water mixtures has been the subject of many investigations, mainly due to the search for alternative energy sources (ethanol). In the past decade a lot of polymers have been screened as a membrane material for this separation problem. Very promising results were obtained using poly(vinylalcohol) (PVA) as the membrane material.

PVA is a polymer that has been investigated intensively as membrane material for various processes, such as dialysis [3.7-3.9], controlled drug release [3.10-3.13,3.30] and reverse osmosis [3.15-3.30]; in the case of reverse osmosis also the separation of ethanol/water has been investigated [3.17,3.18]. Recently PVA was studied for the separation of gases [3.31,3.32]. A great advantage of PVA is the chemical stability with respect to organic liquids, especially when PVA membranes are crosslinked [3.19-3.21].

Already in 1961 Schrodt et al [3.33] reported on the separation of organic liquid mixtures by pervaporation using PVA membranes. In 1962 Binning et al [3.5] patented the use of homogeneous PVA membranes for the dehydration of organic liquids by pervaporation. Later also Huang et al [3.6,3.7] presented results on the dehydration of ethanol using homogeneous (modified) PVA membranes. In 1983 the Japanese company Kuraray patented a combination of distillation and the pervaporation process for the dehydration of ethanol, using PVA hollow fiber membranes [3.34], although nothing has been published afterwards on the preparation and properties of these membranes.

It took until 1983 before a membrane [3.14] was developed that could be used in a commercial installation [3.36]. This membrane is a composite membrane, with a selective toplayer of crosslinked PVA. Because the mechanism for transport in this membrane was not clearly understood, a large part of the effort in pervaporation research was shifted to the investigation and possible applications of homogeneous PVA membranes, as seen from the numerous presentations on this subject during pervaporation conferences in Atlanta (1986) and San Antonio (1987) and publications in literature [3.37-3.41].

In the previous chapter the solution-diffusion model has been discussed, which is generally used to describe transport of liquids through dense polymer membranes during pervaporation. It was shown by model calculations that the pervaporation properties of the membranes can be influenced by crosslinking or by changing the crystallinity of the membrane, because both sorption and diffusion are influenced. In literature the effect of crosslinking on sorption in PVA membranes has been reported [3.21,3.42]. In this chapter the influence of crystallinity on pervaporation properties of homogeneous PVA membranes will be investigated.

The crystallinity of PVA membranes, prepared by evaporation of a solvent from a casted film, can be influenced in several ways.

The crystallinity is strongly dependent on the degree of hydrolysis of PVA. PVA is usually prepared by hydrolysis of poly(vinylacetate) (PVAc). By partial hydrolyzation (co-)polymers are obtained with both hydroxyl and acetate groups. Because the chain structure of fully hydrolyzed PVA is very regular, this polymer is semi-crystalline. In partially hydrolyzed polymers the acetate groups disturb the regular structure, giving less possibility for crystallization. Another effect of an increasing amount of acetate groups is a decrease of hydrophilicity of the polymer. Whereas the hydroxyl groups in PVA can act as donor to hydrogen bonds, the acetate groups do not have that possibility.

The crystallinity of PVA membranes can also be influenced by variation of the evaporation rate of the solvent [3.43] or by applying a heat-treatment [3.13,3.44-3.46]. Especially this last method has widely been used to influence the properties of PVA membranes. The main purpose of a heat-treatment was to improve the stability of the membranes in aqueous mixtures, or to increase the rejection in reverse osmosis [3.5,3.26,3.48,3.51]; in most cases the permeability decreased due to the heat-treatment.

In this chapter the influence of the degree of hydrolysis on the crystallinity, and on the sorption and pervaporation characteristics of ethanol/water mixtures in homogeneous PVA membranes (without heat-treatment) will be investigated. Furthermore, the influence of a heat-treatment on the pervaporation results will be discussed.

3.2 Preparation of PVA membranes

Due to the regular chain structure of fully hydrolyzed PVA, the polymer can crystallize easily. The hydroxyl groups in the polymer can form intermolecular hydrogen bonds. For the preparation of membranes, PVA has to be dissolved in a solvent that can break these hydrogen bonds, and dissolve the crystallites. Good solvents for PVA are water and dimethylsulfoxide (DMSO), but the crystallites only dissolve at elevated temperatures: whereas solutions in DMSO can be obtained at 60°C, aqueous solutions have to be heated up to about 90°C. Upon cooling the solutions to room temperature no recrystallization occurs, due to strong solvatation of the polymer. After casting the solution on a support (perspex or glass) the solvent can be evaporated for the preparation of homogeneous membranes. Upon removal of the solvent the polymer recrystallizes again, and a semi-crystalline membrane is obtained finally.

Although these membranes can be used in aqueous systems at low temperatures without any post-treatment (due to the presence of crystallites), the stability against water and organic solvents at higher temperatures can be increased by crosslinking. This can be performed by:

- applying a heat-treatment: etherification of hydroxyl groups in PVA [3.49]. Although this reaction is possible as a result of a heat-treatment, crystallization may occur too.
- using crosslinking agents, such as: (di-)aldehydes [3.10-3.14,3.21,3.22,3.50-3.54], ketones [3.21,3.52], dicarboxylic acids [3.14,3.17,3.21,3.24,3.52], anhydrides, metal ions [3.19-3.21, 3.24,3.28,3.29,3.47,3.52] and di-isocyanates [3.55].
- reactions induced by radiation [3.25,3.42,3.45,3.56-3.58].

These crosslinking procedures have been applied for the preparation of homogeneous and of asymmetric membranes [3.13,3.18-3.24,3.52], mostly in a flat configuration, but also for hollow fiber membranes [3.8,3.51,3.59].

3.3 Experimental

3.3.1 Materials

Four types of poly(vinylalcohol) with different degrees of hydrolysis have been used: 88%, 96%, 98% and 100%. These types are represented by PVA-96-88, PVA-95-96, PVA-126-98 and PVA-115-100 respectively, and are listed in table 3.1. Maleic acid (general purpose grade) was obtained from BDH Chemicals Ltd. Ethanol (analytical grade) was used without further purification; water was ultrafiltrated before use.

Table 3.1: Types of poly(vinylalcohol) used for the preparation of homogeneous membranes.

polymer	M_w (Dalton) *	degree of hydrolysis *	supplied by
PVA-96-88	96,000	88%	Aldrich
PVA-95-96	95,000	96%	Aldrich
PVA-126-98	126,000	98%	Aldrich
PVA-115-100	115,000	100%	Aldrich

** given by the manufacturer.*

3.3.2 Membrane preparation

Casting solutions were prepared by dissolving PVA in water (10 w% or 12.5 w%). Upon heating to about 90°C a clear solution was obtained. For the preparation of crosslinked PVA membranes 0.05 mole maleic acid per mole monomeric unit of PVA was added to the cold casting solution. Homogeneous membranes were prepared by casting the solution on a perspex plate.

The solvent was removed by evaporation in a nitrogen atmosphere at room temperature. In some cases the membranes were exposed to a heat-treatment after the evaporation of the solvent was completed. The membranes, covered in a petri-dish, were placed in an air-vented oven for 10 or 30 minutes, at temperatures of 130°C or 150°C. This heat-treatment was also applied in the case of crosslinking the membranes with maleic acid. Before the membranes were used in the pervaporation experiments, the membranes were pre-swollen in the respective feed mixtures at 25°C.

3.3.3 Differential Scanning Calorimetry

A Perkin Elmer Differential Scanning Calorimeter (DSC) in combination with a System 4 Microprocessor Controller and a Thermal Analysis Data Station (TADS) Model 3700 was used for DSC measurements. Nitrogen gas was purged through the sample chambers. The polymer samples were placed in aluminium sample pans, which were sealed with perforated covers. The runs were performed from 50°C till 260°C, using a constant heating rate of 40°C/min. unless stated otherwise. The melting enthalpy and the onset of melting of the samples were calculated by the TADS system. The system was calibrated using Indium.

Table 3.2: Literature data for the heat of fusion ΔH_f of PVA. Average ΔH_f= 1.65 kcal/mole= 37.5 cal/g.

method *	heat of fusion ΔH_f (kcal/mole)	reference
Copolymer	0.56	[3.62]
Diluent	1.05	[3.63]
Diluent	1.43	[3.62]
Diluent	1.47	[3.62]
Copolymer	1.57	[3.62]
Diluent	1.64	[3.62]
Copolymer	1.67	[3.62]
Diluent	2.00	[3.62]
Diluent	2.47	[3.62]
Diluent	2.63	[3.35]

* *In the 'copolymer method' the melting temperature of a semi-crystalline polymer is determined as a function of the composition of the copolymer. In the 'diluent method' the melting temperature of the polymer is determined as a function of the concentration of an absorbed liquid in the polymer. For both methods the heat of fusion is calculated using thermodynamic equations.*

The enthalpy of melting ΔH^* (latent heat) of a semi-crystalline polymer can be related to the overall crystallinity ϕ_c of the polymer, if the enthalpy of melting for 100% crystalline material ΔH_f (heat of fusion) is known: $\phi_c = \Delta H^*/\Delta H_f$. In literature scattered data (see table 3.2) have been reported for the heat of fusion for PVA, because this parameter can only be determined by indirect methods. We used the average value of the heat of fusion from table 3.2 to estimate the crystallinity of our samples: ΔH_f=1.65 kcal/mole=37.5 cal/g, using the molecular weight of a monomeric unit of fully hydrolyzed PVA. The melting enthalpies of PVA powders as well of homogeneous membranes of PVA with different degrees of hydrolysis have been determined.

3.3.4 Sorption experiments

Equilibrium sorption experiments were performed at 25°C, using thick strips (thickness between 50 and 200 µm, dry weight of about 0.3 g.) of homogeneous PVA membranes (without heat-treatment). The total sorption and the preferential sorption of ethanol/water mixtures in these membranes were determined at 50 w%, 90 w% and 100 w% ethanol, for PVA with different degrees of hydrolysis. All experiments were performed in triplo, and the three results were averaged.

The experimental method is described in chapter 2 of this thesis. The total sorption is represented by Q: grams of absorbed liquid per gram dry polymer. The sorption results can also be presented by the component sorption data. From the total sorption Q and the composition of the liquid absorbed in the membrane the component sorption of water (Q_w) and ethanol (Q_e) is calculated: $Q_w=Q.c_w^m$ and $Q_e=Q.c_e^m$ (with $c_w^m+c_e^m=1$). The preferential sorption is represented by the equilibrium sorption selectivity α^s, which is calculated from the liquid composition of the feed (f) and the composition of the absorbed liquid in the membrane (m), according to:

$$\alpha^s = (c_w^m/c_e^m)/(c_w^f/c_e^f) \qquad (1)$$

The composition of the liquids was determined by gas chromatography.

3.3.5 Pervaporation experiments

The pervaporation experiments were performed employing two stirred glass cells, as described by Mulder et al [3.60]. The effective membrane areas in the cells are 71 cm^2 and 80 cm^2. The pressure at the downstream side was kept below 500 Pa by a vacuum pump. The permeate was collected in cold traps, which were cooled by liquid nitrogen. Fluxes were determined every hour during eight hours by determination of the weight increase of the cold traps. The pervaporation properties are characterized by the flux J and the pervaporation selectivity α^p.

The fluxes of the different membranes were mostly normalized to a membrane thickness of 10 µm, assuming a proportionality between the flux J and the reciprocal membrane thickness 1/d: J_n=J.d/10 (kg/m^2h).

The fluxes can also be presented by the component flux data. From the total flux J_n and the composition of the permeate, the component fluxes of water ($J_{n,w}$) and ethanol ($J_{n,e}$) are calculated: $J_{n,w}=J_n \cdot c_w^p$ and $J_{n,e}=J_n \cdot c_e^p$ (with $c_w^p+c_e^p=1$).

The pervaporation selectivity α^p was calculated from the liquid composition of the feed (f) and the permeate (p) according to equation (2). Unless stated otherwise, α^p is assumed to be independent of the membrane thickness within the range of thicknesses used.

$$\alpha^p = (c_w^p/c_e^p)/(c_w^f/c_e^f) \qquad (2)$$

The thickness of the dry membranes varied between 4 and 63 µm. The composition of the liquids was determined by gas chromatography.

3.4 Results and discussion

3.4.1 Differential Scanning Calorimetry

DSC experiments were performed to obtain information about the extent of crystallinity of the various PVA membranes that were used for the sorption and pervaporation experiments.

It is known that the crystallinity of PVA can be increased by a heat-treatment at temperatures roughly above 100°C [3.13,3.44-3.46]. Because during a DSC run the temperature of the sample is raised from 50°C till 260°C, crystallization of the sample during the run is possible. As a result the crystallinity, determined in this way, can be higher than that of the original sample (before the run). It was investigated whether the crystallinity of PVA powders increased during a DSC run using a heating rate of 40°C/min., by using a different heating procedure. Whereas in the normal DSC runs a constant heating rate of 40°C/min. was used, in the second procedure the samples were heated to a temperature just below the onset of melting, using a maximum heating rate (200°C/min.); the runs were then completed using the normal heating rate of 40°C/min. The enthalpies of melting monitored in these two procedures did not differ significantly from each other. Hence, it is concluded that the crystallinity of the samples does not increase during the DSC runs, using a heating rate of 40°C/min.

The thermograms of the DSC runs for the *PVA powders* are given in figure 3.1. The small vertical lines in the thermograms indicate the integration boundaries. These boundaries were set to the temperature where the recorded signal deviated significantly from a straight line.

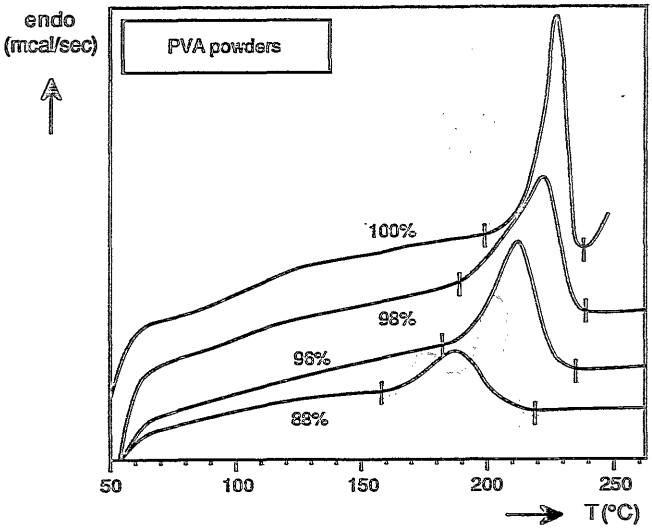

Figure 3.1: Thermograms of DSC runs for PVA powders, with different degrees of hydrolysis: 88%, 96%, 98% and 100%. Heating rate: 40°C/min.

The enthalpies of melting ΔH* of the different samples are given in table 3.3. The enthalpy of melting decreases with decreasing degree of hydrolysis. Whereas the presence of 2% of acetate groups in PVA-126-98 does not influence the crystallinity compared to fully hydrolyzed PVA (PVA-115-100) significantly, the crystallinity of PVA-95-96 (4% acetate groups) is about 10% lower, and the crystallinity of PVA-96-88 is about 50% lower. Using the average value from literature of 37.5 cal/g for the heat of fusion ΔH_f, the crystallinity of the PVA powders varied between ϕ_c=23% for PVA-96-88 and ϕ_c=46% for PVA-115-100.

Table 3.3: Melting enthalpy and onset of melting from DSC experiments for PVA powders and homogeneous PVA membranes. Heating rate: 40°C/min.

sample	*powder*		*membrane*	
	ΔH* (cal/g)	onset (°C)	ΔH* (cal/g)	onset (°C)
PVA-115-100	17.4 ± 0.5	216	13.2 ± 0.1	211
PVA-126-98	17.2 ± 0.1	202	12.7 ± 0.6	203
PVA-95-96	15.7 ± 0.9	198	11.3 ± 0.4	192
PVA-96-88	8.8 ± 0.1	166	11.2 ± 0.2	149

In figure 3.2 the thermograms of the DSC runs for the *PVA membranes* are given; the enthalpies of melting ΔH* are also given in table 3.3. The same trend is found as for the PVA powders:

the highest crystallinity is found for the fully hydrolyzed PVA (ϕ_c=35%), and the crystallinity decreases with decreasing degree of hydrolysis. This decrease, however, is much smaller in comparison with that for the powders; whereas the crystallinity of the three membrane samples with a high degree of hydrolysis is smaller compared to the powder, the crystallinity of the PVA-96-88 membrane is higher than that of the powder (ϕ_c=30% and ϕ_c=23% respectively).

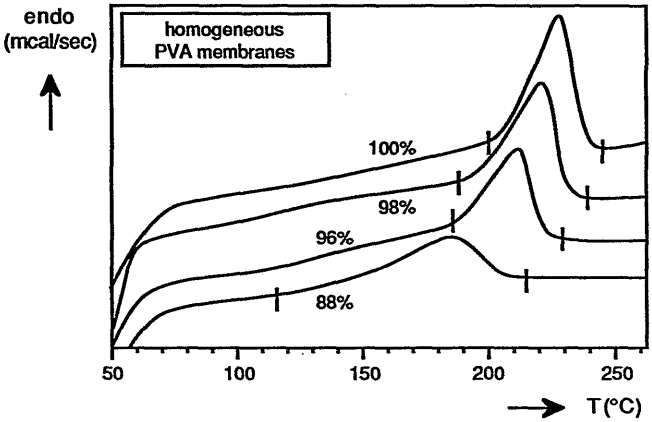

Figure 3.2: Thermograms of DSC runs for homogeneous PVA membranes, with different degrees of hydrolysis: 88%, 96%, 98% and 100%. Heating rate: 40°C/min.

This relatively high crystallinity of the PVA-96-88 membrane is rather surprising. As can be seen from the corresponding thermogram in figure 3.2, the high melting enthalpy of this sample is due to the lower temperature where the crystallites start to melt: whereas in the powder melting starts roughly at about 160°C, the crystallites in the membrane already melt at about 115°C.

Furthermore, it is surprising that the crystallinities of the membranes are lower than that of the corresponding powders, except for the 88% hydrolyzed PVA. Crystallization phenomena are determined by nucleation and growth of crystallites. Powders are generally prepared by precipitation from a dilute solution, in which case the molecular structure is frozen within a short period of time. Although many crystallites can be nucleated, there is little time for growth of the crystallites. Because membranes are prepared by slow evaporation of the solvent, there is more time for growth of the crystallites, resulting in a higher crystallinity compared to powders. Only in the case of the 88% hydrolyzed PVA a higher crystallinity was found for the membrane. The lower crystallinity of the other membranes must be due to other effects.

Summarizing the DSC results, it is concluded that all PVA membranes were semi-crystalline.

The 100% hydrolyzed PVA contains the largest amount of crystallinity, whereas at decreasing degree of hydrolysis the crystallinity decreased to some extent.

3.4.2 Influence of the degree of hydrolysis on pervaporation and sorption results for PVA membranes

To investigate the mechanism for transport of ethanol/water mixtures in PVA membranes, equilibrium sorption and pervaporation experiments have been performed at 25°C, using the same membranes. To take into account the effect of crystallinity, polymers with different degrees of hydrolysis were used: 88%, 96%, 98% and 100%. Because PVA membranes generally will be applied at high ethanol concentration, three ethanol/water mixtures were used as a feed: 50 w%, 90 w% and 100 w% ethanol. The sorption and pervaporation properties of the PVA-96-88 membranes could not be determined in a 50 w% ethanol/water mixture, because the membranes dissolved in this mixture.

Although in some experiments pure ethanol (reagent grade: >99.8 w% ethanol; no water could be detected with gas chromatography) was used as a feed, both the permeate in the pervaporation experiments and the liquid distilled from the membrane in the sorption experiments contained water. The sorption and permeation of water has to be the result of the presence of traces of water in the 'pure ethanol' in the feed, which is an indication of the high sorption and pervaporation selectivities for water at high ethanol concentrations.

Pervaporation

In figure 3.3 the pervaporation results are given as a function of the feed composition, for different degrees of hydrolysis of PVA. Figure 3.3a clearly shows that for high ethanol contents in the feed low fluxes are obtained using the highly hydrolyzed PVA membranes. When the water content in the feed is increased, fluxes increase strongly for all types of PVA. The selectivities of all membranes increase with increasing ethanol content in the feed (see figure 3.3b). This increase in selectivity is caused by a strong decrease in the component flux of ethanol with increasing ethanol content in the feed, as can be seen from figure 3.4. Because component fluxes in pervaporation generally increase if the concentration of the component in question in the feed is increased, this behaviour of the component flux of ethanol must be due to coupling phenomena: for increasing water content in the feed the component flux of ethanol is strongly enhanced by the increase of the component flux of water. This behavior of the component flux of ethanol as a function of the concentration has also been reported by Bakish et al [3.61] for GFT membranes (crosslinked PVA).

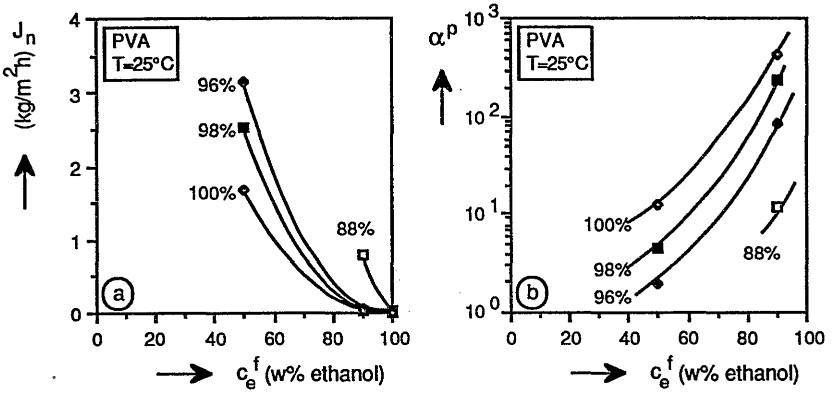

Figure 3.3: Normalized pervaporation flux J_n (a) and pervaporation selectivity α^P (b) for homogeneous PVA membranes, as a function of the ethanol content in ethanol/water mixtures, for PVA with different degrees of hydrolysis. Membrane thickness: 22-25 µm.

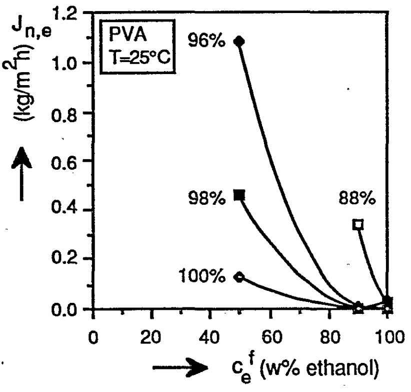

Figure 3.4: Normalized component flux of ethanol $J_{n,e}$ through homogeneous PVA membranes, as a function of the ethanol content in ethanol/water mixtures, for PVA with different degrees of hydrolysis. Membrane thickness: 22-25 µm.
(Note the difference in vertical scale values, compared to figure 3.3a)

Sorption

In order to obtain more information on the separation mechanism, equilibrium sorption experiments were performed. In figure 3.5 the sorption results are given as a function of the feed composition, for different degrees of hydrolysis of PVA. The decrease in the component sorption of water Q_w in figure 3.5a with increasing ethanol content in the feed will lead to a decrease in component flux of water with increasing ethanol content. As can be seen from figure 3.5b the solubility of ethanol in these membranes is very small, except for the 88% hydrolyzed PVA.

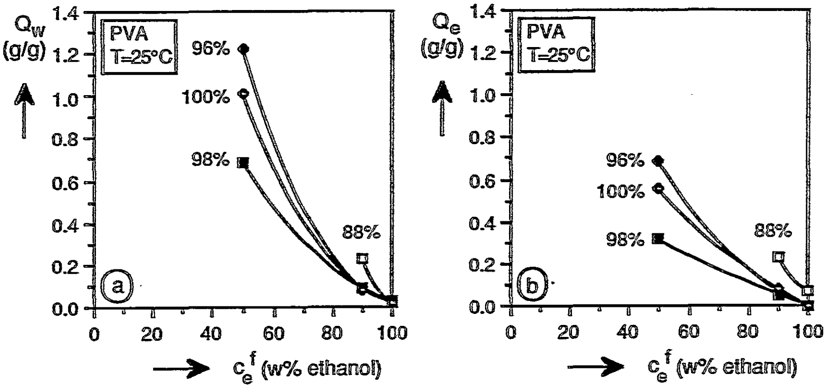

Figure 3.5: Component sorption of water Q_w (a) and of ethanol Q_e (b) in homogeneous PVA membranes, as a function of the ethanol content in ethanol/water mixtures, for PVA with different degrees of hydrolysis.

These results can explain the low flux values for pure ethanol, as given in figure 3.4. When the ethanol content in the feed mixture is decreased, both the component sorption of water Q_w and ethanol Q_e increase. This increase of Q_e with decreasing ethanol concentration can explain the dependence of the component flux of ethanol as a function of the feed concentration as shown in figure 3.4; it must be attributed to the presence (absorption) of water. This can be considered as a thermodynamic coupling phenomenon, which is demonstrated more clearly in figure 3.6. The component sorption of ethanol is plotted here as a function of the component sorption of water: Q_e is linearly dependent on Q_w. From the slope of this figure it can be calculated that the sorption of 1 gram of ethanol is accompanied by 1.83 gram of water. Substituting the respective molecular weights, this means that one molecule of ethanol is absorbed in the presence of about five (actually 4.67) molecules of water. This value is in close agreement with the value of four molecules of water that Bakish et al [3.61] obtained for the GFT membrane, from flux data. However, it should be kept in mind that the properties of the GFT membrane are determined by a PVA toplayer, which is crosslinked and heat-treated, whereas we used non-treated PVA membranes.

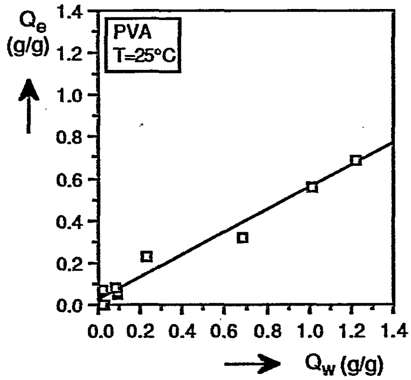

Figure 3.6: Relation between the component sorption of ethanol Q_e and the component sorption of water Q_w in homogeneous PVA membranes.

The coupled sorption of water and ethanol, however, can not explain the results at very low water contents in the feed. In figure 3.7 the component sorption of ethanol and water are given for sorption of 'pure' ethanol in PVA membranes, as a function of the degree of hydrolysis of the PVA. Ethanol is not absorbed at all for the 96%, 98% and 100% hydrolyzed PVA membranes, whereas a significant absorption of water (the 'pure' ethanol feed must have contained traces of water) was found. For the 88% hydrolyzed PVA membrane a rather high component sorption of ethanol was found. However, the component sorption of water is hardly affected by the degree of hydrolysis. Hence, the high component sorption of ethanol here can not be due to the sorption of water (no coupling at high ethanol content in the feed).

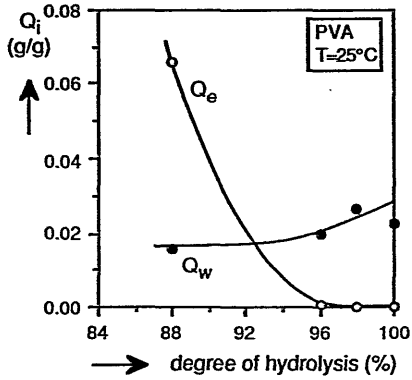

Figure 3.7: Component sorption of ethanol Q_e and of water Q_w from 'pure' ethanol in homogeneous PVA membranes, as a function of the degree of hydrolysis of PVA.

The effect of the degree of hydrolysis on the sorption results of the membranes in pure ethanol can be due to two factors:

a) For lower degrees of hydrolysis the *interaction* between (amorphous) PVA and ethanol is stronger; as a result the ethanol sorption increases in the same direction.
b) For lower degrees of hydrolysis the *crystallinity* of the membranes is lower, which influences the sorption of low molecular weight components in semi-crystalline polymers.

If the absorption of pure ethanol in PVA membranes is only determined by the interaction between amorphous PVA and ethanol, the interaction between ethanol and 100% hydrolyzed PVA must be extremely weak, because this membrane absorbs no ethanol at all. This is not always the case, as was shown in the previous chapter. In that case also fully hydrolyzed PVA membranes were prepared, which absorbed about 8% of pure ethanol. Since the interaction between the polymer and ethanol must be the same, the difference between the ethanol absorption of the membranes in this chapter and the membranes in the previous chapter must be due to differences in crystallinity of the membranes. These possible differences in crystallinity may have originated from the fact that the membranes were prepared from a different casting solution: in the previous chapter DMSO was used, whereas water is used in this chapter.

Furthermore, both the interactions between water and PVA, and ethanol and PVA, are based on the formation of hydrogen bonds. Because ethanol and water do not differ too much in ability to form hydrogen bonds, it is unlikely that there is such a large difference between the interaction of PVA and water, and PVA and ethanol, respectively. Since strong interactions occur between water and PVA (amorphous PVA dissolves in water), the absence of ethanol sorption is rather unexpected if only interaction forces are considered.

Hence, the low sorption of ethanol in highly hydrolyzed PVA membranes should mainly be determined by the factor crystallinity. Crystallinity can be considered as physical crosslinking. In chapter 2 of this thesis it has been shown that the effect of crosslinking (and thus crystallinity) is strongly dependent on the molecular dimensions of the components. For sorption the components must have the opportunity to penetrate into the polymer: there must be 'free volume' available to penetrate. Whereas in crosslinked polymers this free volume is determined by the crosslink density, in the case of semi-crystalline polymers this free volume is determined by the total amount of crystallinity and the number of crystallites. Our DSC experiments indicated that the PVA membranes with a high degree of hydrolysis are about 35% crystalline. Since water is a smaller molecule than ethanol (the molar volumes differ by a factor of 3.2 at 25°C), water is less restricted than ethanol to penetrate into the semi-crystalline polymer. It is even possible that in the case at hand the crystallinity is so high, that pure ethanol can not penetrate at all.

Whereas the low ethanol absorption at high degree of hydrolysis is mainly due to the high crystallinity, the increase of the ethanol sorption with decreasing degree of hydrolysis can also be attributed to the decrease of hydrophilicity of the polymer, as a result of an increase of the amount of more hydrophobic acetate groups. Thus, the interaction between PVA and ethanol becomes stronger with decreasing degree of hydrolysis, which results in an increase of the solubility of pure ethanol in the membranes. Furthermore, the presence of the bulky acetate groups in less hydrolyzed PVA can also create free volume for absorption of ethanol and water.

Summarizing the results, it is concluded that the component sorption of water in PVA membranes increases with increasing water content in the feed. The extremely low solubility of pure ethanol in PVA membranes with a high degree of hydrolysis is mainly due to the high crystallinity of the membranes. Water can be absorbed, mainly because of its smaller molecular size. In aqueous feed mixtures ethanol can only be absorbed as a result of the absorption of water. Due to the absorption of water the membrane swells, and ethanol can then penetrate into the membrane. At decreasing ethanol content in the feed mixture the component sorption of ethanol increases due a coupling effect with the absorption of water.

Sorption versus pervaporation

According to the solution-diffusion model (see chapter 2), the pervaporation properties of homogeneous membranes are determined by sorption and diffusion of the components in the membrane. Hence, the pervaporation selectivity of homogeneous PVA membranes is determined by differences in sorption and diffusion properties of ethanol and water in these membranes. By comparing the sorption and pervaporation selectivities the influence of diffusion can be deduced.

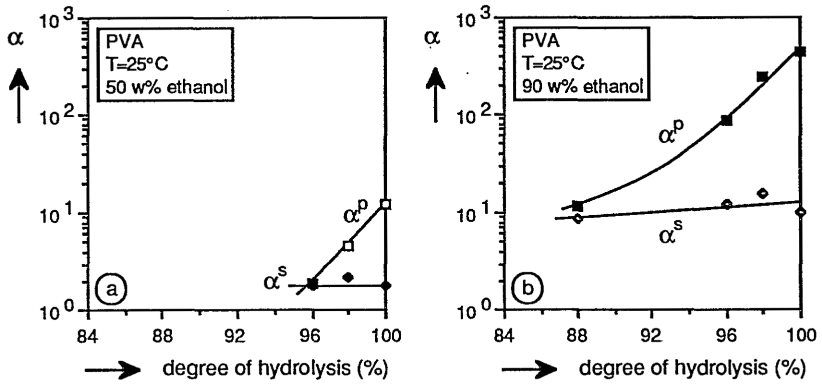

Figure 3.8: Equilibrium sorption selectivity α^S and pervaporation selectivity α^P for homogeneous PVA membranes, as a function of the degree of hydrolysis of PVA, for two feed compositions: 50 w% ethanol (a) and 90 w% ethanol (b) in water.

In the figures 3.8a and 3.8b the equilibrium sorption and pervaporation selectivities are given as a function of the degree of hydrolysis, for two feed compositions. The figures show that, although the pervaporation selectivity is determined to some extent by the sorption selectivity, also diffusion must play an important role.

As already mentioned in the previous chapter, it should be kept in mind that care has to be taken to compare the results from sorption experiments with pervaporation experiments directly, because sorption experiments are equilibrium experiments, whereas pervaporation data are obtained from steady-state experiments. Therefore, the information on diffusion obtained in this way, must be interpreted carefully and has only in a qualitative meaning.

3.4.3 Influence of heat-treatments

From the experiments at 25°C it was concluded that the most selective PVA membranes are those with the highest degrees of hydrolysis: 98% and 100%. At lower degrees the polymer absorbs too much ethanol from the ethanol/water mixtures. For that reason these PVA membranes with high degrees of hydrolysis have been investigated more thoroughly.

Furthermore, it was seen from the experiments at 25°C the properties of PVA membranes depend to a large extent on the crystallinity of the membranes. It is known from literature that the crystallinity of PVA can be increased by applying a heat-treatment. The effect of a heat-treatment of 30 minutes at 150°C on the crystallinity of PVA membranes is demonstrated in table 3.4. The melting enthalpies (determined by DSC) are given for membranes of 98% and 100% hydrolyzed PVA, with and without heat-treatment.

Table 3.4: Influence of a heat-treatment (30 min. at 150°C) on the melting enthalpy for homogeneous PVA membranes, by DSC experiments. Heating rate: 40°C/min.

sample	without heat-treatment ΔH^* (cal/g)	with heat-treatment (30 min. at 150°C) ΔH^* (cal/g)
PVA-115-100	14.5 ± 0.2	17.7 ± 0.2
PVA-126-98	15.6 ± 0.6	17.7 ± 0.2

The table shows that due to the heat-treatment the crystallinity of the membranes increased approximately 14% to 22%. The crystallinity of both types of membranes is similar after the heat-treatment.

In table 3.5 pervaporation results are given for membranes of the same types of PVA (98% and 100% hydrolyzed) for different heat-treatments; the feed concentration was 90 w% ethanol, the temperature 70°C. From the table it is concluded that the reproducibility of the experiments is rather bad: using membranes prepared under the same conditions the fluxes and selectivities vary considerably. If the results are considered qualitatively, it is concluded that only a heat-treatment of 30 minutes at 150°C may result in a significant change of pervaporation properties: the flux decreases and selectivity increases due to this heat-treatment. There is no significant difference between most results of the two types of PVA polymers used. This is due to the fact that the crystallinity of the membranes without heat-treatment is about the same, whereas the effect of the heat-treatment on the crystallinity of both types of membranes is also roughly the same (see table 3.4). Only the PVA-115-100 membranes that were heat-treated during 30 minutes at 150°C gave lower fluxes and higher selectivities compared to the PVA-126-98 membranes with the same heat-treatment. The discrepancy between the DSC results for the membranes without heat-treatment in table 3.3 and table 3.4 is in agreement with the bad reproducibility found for the pervaporation experiments.

Table 3.5: Pervaporation results of homogeneous PVA-126-98 and PVA-115-100 membranes, with different heat-treatments. Membrane thickness: 21-28 µm. Feed: 90 w% ethanol, 70°C.

heat-treatment		PVA-126-98		PVA-115-100	
time (min.)	T (°C)	J_n (kg/m^{2}h)	α^P	J_n (kg/m^{2}h)	α^P
-	-	0.353	102	0.200	88
-	-	0.294	62	0.308	112
-	-	0.322	103		
10	130	0.193	81	0.200	188
10	130	0.207	190	0.230	125
10	130	0.297	133		
30	130	0.154	110	0.132	90
30	130	0.168	73	0.189	160
30	130	0.300	140		
10	150	0.294	120	0.101	165
10	150	0.191	74	0.158	80
10	150	0.216	80	0.252	140
30	150	0.090	125	0.063	200
30	150	0.103	103	0.065	300
30	150	0.159	155	0.099	105

Because the pervaporation results are quite good for these heat-treated membranes (high selectivity and reasonable flux), the influence of membrane thickness was investigated. The casting thickness was varied between 0.05 and 1.0 mm to obtain membranes with a dry thickness between 5 and 65 μm. The membranes were exposed to a heat-treatment of 30 minutes at 130°C, because these membranes have higher fluxes than the membranes heat-treated at 150°C. Two casting solutions were used: 10 w% and 12.5 w% of PVA-126-98 in water. The results are presented in the figures 3.9 and 3.10.

From figure 3.9 it can be seen that the reciprocal flux is proportional to the membrane thickness, which is in agreement with the solution-diffusion model. But, as in table 3.5 the results are again somewhat scattered. There is also no significant difference between the results for the two concentrations of the casting solutions.

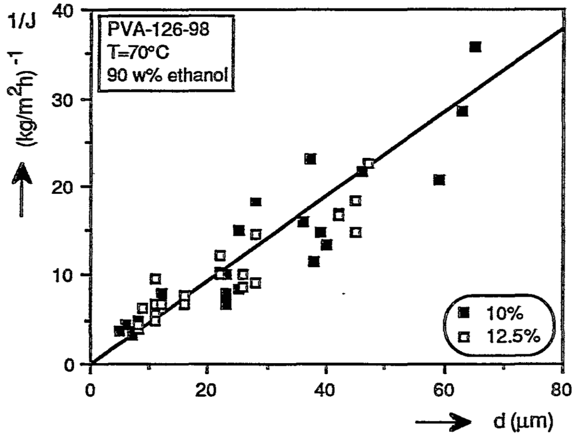

Figure 3.9: Reciprocal flux 1/J for homogeneous PVA membranes, as a function of membrane thickness d, using two casting solutions: 10 w% and 12.5 w% PVA in water. Heat-treatment: 30 min. at 130°C.

In figure 3.10 the selectivity is plotted as a function of the membrane thickness. Again, the results are not very reproducible: for a chosen membrane thickness the selectivity can vary by a factor of more than 5. Whereas most selectivity values are found between 60 and 150, also much higher selectivities were found, surprisingly even for thin membranes. Since the total flux is mainly determined by the component flux of water, these scattered results of the selectivity must be due to the component flux of ethanol. Because the component flux of ethanol is strongly influenced by the crystallinity of the membranes (as was shown in 3.4.2), the heat-treatment is probably not very reproducible, and is causing differences in crystallinity of the membranes.

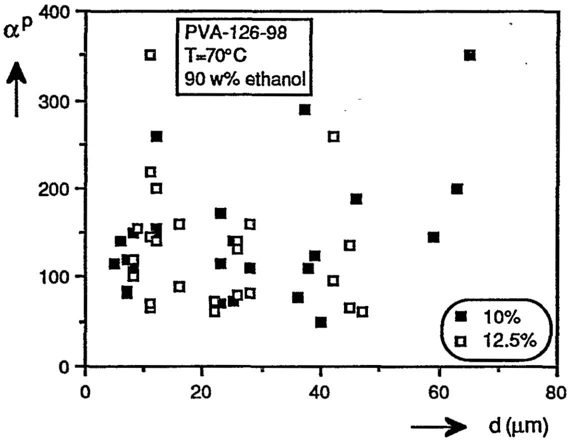

Figure 3.10: Pervaporation selectivity α^P for homogeneous PVA membranes, as a function of membrane thickness d, using two casting solutions: 10 w% and 12.5 w% PVA in water. Heat-treatment: 30 min. at 130°C.

Influence of crosslinking

The pervaporation characteristics of the commercial GFT membrane [3.14] are determined by the PVA toplayer. This toplayer is deposited on a porous support by a coating technique, followed by drying and crosslinking. The crosslinking agent generally is maleic acid, which is added to the coating solution. The crosslinking is achieved by applying a heat-treatment at about 150°C.

In order to investigate the influence of the maleic acid, homogeneous PVA-126-98 membranes have been prepared, where maleic acid was added to the casting solution (10 w% PVA in water). After casting the solution and evaporation of the solvent (water), the membranes were exposed to a heat-treatment of 30 minutes at 150°C. Because the results with other heat-treated PVA membranes were obtained with various membrane thicknesses, the flux and selectivity of the crosslinked membranes were also determined as a function of membrane thickness. The membranes were tested at 70°C with a feed mixture of 90 w% ethanol. The results are presented in figures 3.11 and 3.12.

In figure 3.11 the reciprocal flux is plotted as a function of the membrane thickness. For comparison the flux values (which are not normalized in this case, and are represented by the three open circles) are also shown for comparable PVA membranes (identical heat-treatment) without maleic acid (data taken from table 3.5). As can be seen higher fluxes (by a factor ≈2.5) are obtained when the membranes are crosslinked with maleic acid.

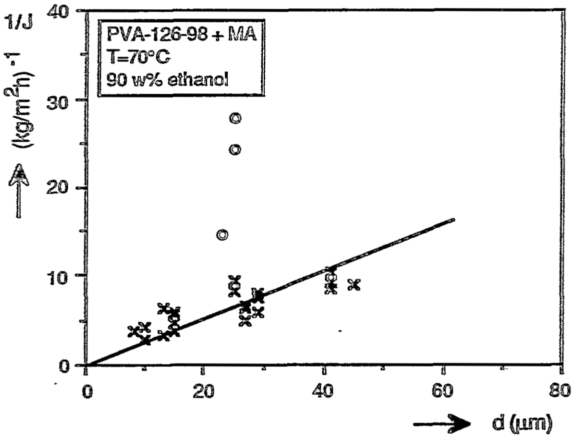

Figure 3.11: Reciprocal flux 1/J for homogeneous PVA membranes, crosslinked with maleic acid (MA), as a function of membrane thickness d; the three open circles represent the results for identically prepared membranes without maleic acid added. Heat-treatment: 30 min. at 150°C.

In figure 3.12 the selectivity is plotted as a function of the membrane thickness. As in the experiments presented before, the results are rather scattered: $45<\alpha^P<125$. These values are comparable to the selectivities of the membranes without maleic acid ($103<\alpha^P<155$, from table 3.5), which are also plotted in this figure (the three open circles).

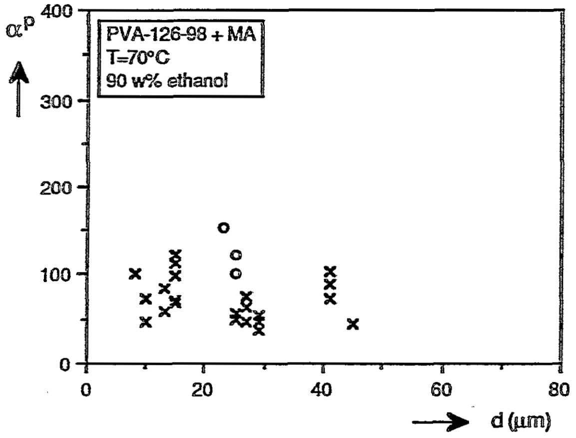

Figure 3.12: Pervaporation selectivity α^P for homogeneous PVA membranes, crosslinked with maleic acid (MA), as a function of membrane thickness d; the three open circles represent the results for identically prepared membranes without maleic acid added. Heat-treatment: 30 min. at 150°C.

Hence, addition of maleic acid to the casting solution results in higher pervaporation fluxes, without a significant loss of selectivity. The presence of maleic acid reduces the crystallinity of the membrane upon evaporation of the solvent. The effect of addition of maleic acid to the casting solution was also studied by DSC experiments, which results are given in table 3.6. In this table the melting enthalpies of homogeneous membranes of PVA-126-98 are given, for membranes with and without maleic acid added, before and after a heat-treatment of 30 minutes at 150°C.

Table 3.6: Influence of a heat-treatment (30 min. at 150°C) on the melting enthalpy for two homogeneous PVA membranes, by DSC experiments. Heating rate: 40°C/min.

sample	without heat-treatment ΔH^* (cal/g)	with heat-treatment (30 min. at 150°C) ΔH^* (cal/g)
PVA-126-98	15.6 ± 0.2	17.7 ± 0.2
PVA-126-98 + maleic acid	12.8 ± 0.3	12.1 ± 0.1

According to this table, addition of maleic acid to the casting solution reduces the crystallinity of the membranes after evaporation: $\Delta H^*=15.6$ cal/g decreases to $\Delta H^*=12.8$ cal/g. This can be explained by the fact that maleic acid is bound to the PVA in the membrane during or after evaporation, either by hydrogen bonding or by a covalent bonding (esterification). This explanation is supported by the absence of the melting peak of pure maleic acid ($T_m \approx 140$°C) in the thermograms of the membranes. Whereas the crystallinity of the membrane without maleic acid is increased after the heat-treatment, the crystallinity of the membrane with maleic acid was not influenced significantly by the heat-treatment. The presence of maleic acid, bound to the PVA chains probably prevents further crystallization of the membrane. As a result of the heat-treatment the membrane is really crosslinked by maleic acid, as it was concluded from the occurrence of an extra endothermic peak at 110°C in the thermograms of the membranes that were not exposed to a heat-treatment. This peak can be the result of the reaction of the second carboxyl group with a hydroxyl group in PVA, leading to a crosslink. Another indication of crosslinking for the PVA membranes with maleic acid is the resistance against boiling water. Whereas normal PVA membranes (without maleic acid added) dissolve in boiling water (even after a heat-treatment), the membranes containing maleic acid did not dissolve.

Concluding, addition of maleic acid to the casting solution results in a lower crystallinity of the membranes upon evaporation (compared to membranes without maleic acid). During the heat-treatment further crystallization is prevented by the presence of bound maleic acid, which crosslinks the PVA covalently at temperatures higher than 110°C. Due to the lower crystallinity higher pervaporation fluxes can be obtained. The selectivity remains at an acceptable level, because the chemical crosslinks prevent the membrane from extensive swelling. Furthermore, the presence of the maleic acid crosslinks can also influence the thermodynamic interactions between the membrane and the permeating components, which will also influence the permeation properties.

Reproducibility

The reproducibility of the pervaporation results presented in the last paragraph was not quite good. Especially the results of the selectivities of the membranes were rather scattered. This bad reproducibility must be due to the preparation method of the membranes. As was shown before, the properties of PVA membranes are strongly influenced by crystallinity. Because during the preparation of the membranes the crystallinity can be influenced by several factors, more attention was paid to the reproducibility of the membrane preparation. The crystallinity of a membrane that is heat-treated is determined by two factors: the crystallinity of the membrane before the heat-treatment, and the increase of crystallinity of the membrane due to the heat-treatment. To examine which factor mainly causes non-reproducible results, the reproducibility of non heat-treated membranes was investigated. Membranes were prepared under exactly the same conditions: the same casting solution was used, the evaporation times were identical, all dry membranes were preswollen in a 90 w% ethanol solution. From each evaporated film two membranes were cut, which were used for pervaporation experiments. The pervaporation results for a feed of 90 w% ethanol at 70°C are given in the tables 3.7 and 3.8, for two types of PVA. Whereas both the flux and the selectivity of the two membranes from the same film are more or less identical, also the reproducibility of results of the 4 different films is good.

Table 3.7: Pervaporation results of doublets of homogeneous PVA-126-98 membranes. No heat-treatment. Feed: 90 w% ethanol, 70°C.

d (µm)	J_n (kg/m^{2}h)	α^p
22	0.378	85
22	0.392	81
23	0.363	93
23	0.481	78
25	0.383	88
25	0.433	81
26	0.377	92
26	0.385	91

Table 3.8: Pervaporation results of doublets of homogeneous PVA-115-100 membranes. No heat-treatment. Feed: 90 w% ethanol, 70°C.

d (µm)	J_n (kg/m^{2}h)	α^p
22	0.455	73
22	0.495	86
22	0.288	110
22	0.328	112
23	0.458	91
23	0.478	84
23	0.380	86
23	0.221	89

From these results it is concluded that pervaporation results for homogeneous PVA membranes are very sensitive to different steps in the membrane preparation method. In order to get reproducible pervaporation results, the membranes have to be prepared, treated and tested under exactly identical conditions.

Summary of pervaporation results using heat-treated PVA membranes

In figure 3.13 all pervaporation results are summarized using heat-treated homogeneous PVA

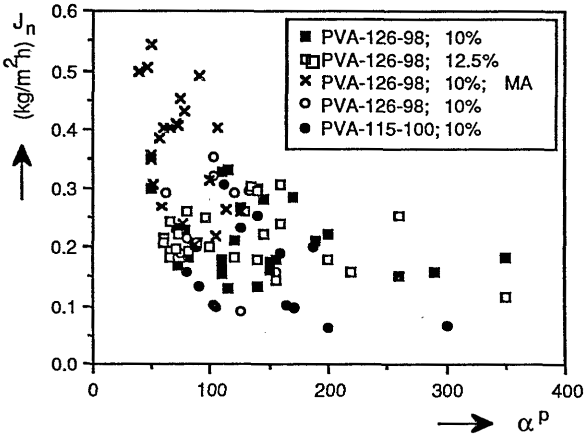

Figure 3.13: Summary of the pervaporation experiments using homogeneous PVA membranes, that were exposed to different heat-treatments. Feed: 90 w% ethanol in water, 70°C.

membranes, for the dehydration of 90 w% ethanol at 70°C. As can be seen from this figure, reasonable fluxes can be obtained at high selectivities. The highest fluxes were found for membranes with maleic acid added to the casting solution.

3.5 Conclusions

Homogeneous PVA membranes with high degrees of hydrolysis can be used for the separation of ethanol/water mixtures by pervaporation, without necessarily applying a crosslinking or heat-treatment. The membranes do not dissolve in aqueous mixtures, due to a considerable amount of crystallinity, which can be considered as physical crosslinks. A high preferential sorption of water from ethanol/water mixtures in these membranes is due to the relatively extremely low sorption of ethanol. This low sorption of ethanol is caused by the high degree of crystallinity of the membranes. Ethanol is only absorbed in the presence of water, which does absorb more easily into the membranes, because of its smaller molecular dimensions.

Due to this low ethanol sorption, the component flux of ethanol from ethanol-rich feed mixtures is also very low, especially for high degrees of hydrolysis of PVA. As a result high selectivities are obtained in pervaporation. This selectivity decreases with a decreasing degree of hydrolysis of PVA, due to a decrease in crystallinity.

A heat-treatment generally results in lower fluxes and higher selectivities, but significant effects are observed only for a heat-treatment of 30 minutes at 150°C.

If maleic acid is added to the PVA casting solution, and a heat-treatment of 30 minutes at 150°C is applied, higher fluxes and comparable selectivities are obtained, compared to membranes without maleic acid added.

3.6 List of symbols

c_i = weight fraction of component i in the liquid (feed, permeate, membrane) (g/g)
d = membrane thickness (μm)
ΔH_f = heat of fusion of a polymer (cal/g)
ΔH^* = melting enthalpy of a semi-crystalline polymer (cal/g)
J = total pervaporation flux (kg/m^{2}h)
J_i = pervaporation flux of component i (kg/m^{2}h)
J_n = total pervaporation flux, normalized to 10 μm membrane thickness (kg/m^{2}h)
M_w = weight averaged molecular weight of the polymer (Dalton)
Q = total sorption in the polymer: grams of absorbed liquid/gram dry polymer (g/g)
Q_i = component sorption of i in the polymer: gram absorbed i/gram dry polymer (g/g)
T = temperature (°C)

α = selectivity (equilibrium sorption, pervaporation, diffusion) (-)
ϕ_c = crystalline fraction of the polymer (-)

subscripts
e = ethanol
w = water

superscripts
d = diffusion
f = feed
m = membrane
p = permeate, pervaporation
s = sorption

3.7 References

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Chapter 4

Pervaporation of ethanol/water mixtures using homogeneous poly(acrylonitrile) membranes.

J.W.F. Spitzen, M.H.V. Mulder, C.A. Smolders

Summary

Homogeneous membranes of poly(acrylonitrile) (PAN) were prepared and tested for the dehydration of ethanol/water mixtures by pervaporation. The selectivities for water were extremely high, but the fluxes were too low to make the membranes interesting for commercial applications. To increase the flux through the membranes, the membrane thickness can be reduced and the feed temperature can be increased. The influence of membrane thickness and feed temperature on the pervaporation results was investigated. By decreasing the membrane thickness the fluxes were increased to acceptable values, but the selectivities decreased strongly for membranes with a thickness less than 20 μm. Some possible explanations for this phenomenon are discussed. The selectivities of thin membranes could be increased by modification of the membrane preparation method. By increasing the feed temperature both fluxes and selectivities could be increased. Polymer relaxation phenomena turned out to be of large importance during the experiments.

4.1 Introduction

Since the increasing interest in membrane technology many polymers have been studied for the development of permselective membranes. Whereas in the beginning of the sixties mostly cellulose derivatives and polyolefines were used, later also other (bulk) polymers have been developed and screened as a membrane material. For some special applications new polymers were synthesized (e.g. by copolymerization), existing polymers were modified by chemical reactions (introduction of functional groups) or grafting, and polymer blend membranes were developed. Poly(acrylonitrile) (PAN) provides some important advantages compared with other polymers for membrane manufacturing. PAN is a rather inert polymer that is resistant to mineral acids and many organic solvents, such as aromatic hydrocarbons, chlorinated hydrocarbons and aliphatic hydrocarbons (PAN can be dissolved in dimethylsulfoxide, dimethylformamide or dimethylacetamide). This resistance to many organic solvents makes PAN a good candidate as a film forming material for membrane separation processes. Another advantage is that PAN is a very common bulk polymer, which is available at low prices. Finally, membrane manufacturing is rather simple: membranes can easily be made by solution casting (homogeneous membranes) or by the phase inversion process (asymmetric membranes).

PAN turned out to be a polymer from which very selective membranes can be prepared to dehydrate ethanol/water mixtures by pervaporation. Extremely high selectivities for PAN homopolymer [4.1-4.3] and copolymers [4.4-4.14] have been reported in literature. Mulder et al [4.1] showed that the preferential permeation of water from ethanol/water mixtures through homogeneous PAN membranes is mainly due to the high preferential sorption of water. Reasons hereto are the smaller molar volume of water (compared to ethanol) and the strong hydrogen bonding forces between water and the nitrile groups [4.15] in PAN. Although hydrogen bonding between PAN and ethanol is also possible, it can be expected that water has more favourable possibilities to form hydrogen bonds with the nitrile groups. Because in a dense PAN membrane the nitrile groups are very close to each other, it is possible that one water molecule forms two hydrogen bonds with different nitrile groups. This hydrogen bridging can also involve a number of water molecules (clusters) [4.16]. An ethanol molecule can only form one hydrogen bond with a nitrile group. Some possibilities for hydrogen bonding of PAN with water or ethanol are given schematically in figure 4.1.

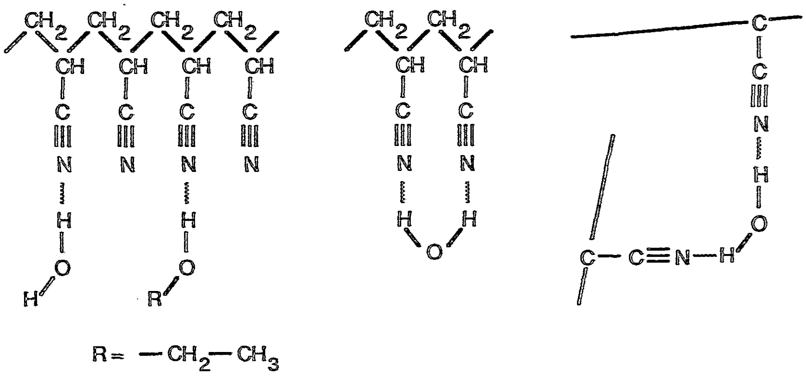

Figure 4.1: Possible hydrogen bond formations between PAN and water, respectively ethanol.

Although the pervaporation selectivity of non-porous PAN membranes for ethanol/water mixtures is extremely high, unfortunately the permeability is very low. There are several methods to increase the fluxes:

a) Changing the chemical structure of the *polymer material*. This can be achieved by chemical modification of the polymer (introduction of specific functional groups, hydrogenation, hydrolysis), by using copolymers [4.4-4.14] or by using blends of PAN with a more permeable polymer [4.17].

b) Changing the *membrane* itself, e.g. by changing the preparation method (influencing the membrane morphology) or by changing the membrane thickness (diffusional flows are proportional to reciprocal diffusion length).

c) Changing the *feed conditions*, such as the feed temperature (diffusion rates increase exponentially with temperature), the feed composition, and the mass transfer of the components in the feed towards the membrane.

In chapter 5 one aspect of the first method a) will be elaborated (blending of PAN with a more permeable polymer), whereas in this chapter the other two methods will be described. The two most important factors influencing the fluxes through homogeneous membranes are the membrane thickness and the feed conditions (especially the feed temperature).

4.2 Experimental

4.2.1 Materials

Poly(acrylonitrile) (PAN) was obtained from Du Pont (PAN-A; M_w=516,000 Dalton). Dimethylformamide (DMF) (reagent grade) and ethanol (analytical grade) were used without further purification; water was ultrafiltrated before use.

4.2.2 Membrane preparation

Casting solutions were prepared by dissolving PAN in DMF (10-20 w%). Homogeneous membranes were prepared by casting the solution on a glass plate. The solvent was removed by evaporation in a nitrogen atmosphere, usually at room temperature, in some cases at elevated temperatures.

4.2.3 Pervaporation experiments

The pervaporation experiments were performed employing two stirred glass cells, as described by Mulder et al [4.18]. The effective membrane areas in the cells are 71 cm^2 and 80 cm^2. The pressure at the downstream side was kept below 500 Pa by a vacuum pump. The permeate was collected in cold traps, which were cooled by liquid nitrogen. Fluxes were determined every hour during eight hours by determination of the weight increase of the cold traps. Experiments were usually performed with a liquid feed mixture of 90 w% ethanol in water, at 70°C. The pervaporation properties are characterized by the flux J and the pervaporation selectivity α^p.

The fluxes of the different membranes were mostly normalized to a membrane thickness of 10 µm, assuming a proportionality between the flux J and the reciprocal membrane thickness 1/d: $J_n=J.d/10$ (kg/m^{2}h).

The fluxes can also be presented by the component flux data. From the total flux and the composition of the permeate, the component fluxes of water (J_w) and ethanol (J_e) are calculated: $J_w=J.c_w^p$, and $J_e=J.c_e^p$ (with $c_w^p+c_e^p=1$).

The pervaporation selectivity α^p was calculated from the liquid composition of the feed (f) and the permeate (p) according to equation (1). Unless stated otherwise, α^p is assumed to be independent of the membrane thickness within the range of thicknesses used.

$$\alpha^p= (c_w^p/c_e^p)/(c_w^f/c_e^f) \qquad (1)$$

The thickness of the dry membranes varied between 3 and 100 µm. The composition of the liquids was determined by gas chromatography.

4.3 Results and discussion

4.3.1 Influence of the membrane thickness on flux and selectivity

Transport in homogeneous, non-porous membranes is usually described by a solution-diffusion model [4.19], which is discussed in chapter 2 of this thesis. This model, originally developed for reverse osmosis, is also accepted to describe transport during pervaporation. According to this model, the components are absorbed in the membrane at the feed side of the membrane, diffuse through the polymer membrane due to an activity gradient, and desorb into a vapour phase at the permeate side. It is generally assumed that the diffusion step is the rate-determining step. The component fluxes are described by Fick's law of diffusion:

$$J_i = - D_i.dc_i^m/dx \qquad (2)$$

In this equation D_i is the diffusion coefficient of component i, which generally is dependent on the concentration of both components in the membrane. It can easily be shown that, independent of the mathematical description of the concentration dependence of the diffusion coefficients (constant, linear or exponential), integration of this equation leads to equations in which the component fluxes J_i are proportional to the reciprocal membrane thickness 1/d. Since for a binary liquid feed both component fluxes are proportional to the reciprocal thickness, also the *total flux J* will be proportional to the reciprocal thickness. Thus, the obvious way to increase fluxes through homogeneous membranes is to decrease the membrane thickness.

The pervaporation selectivity (for fixed feed conditions) is determined by the ratio of the permeate concentrations (equation (1)), hence the selectivity is determined by the ratio of the component fluxes. Because the ratio of the component fluxes is independent of membrane thickness, also the selectivity should be independent of the thickness. This leads to the conclusion that according to the solution-diffusion model fluxes through homogeneous pervaporation membranes can be increased by decreasing the membrane thickness, without loss of selectivity. For the dehydration of ethanol/water mixtures this should make PAN as selective layer in asymmetric and composite membranes rather promising.

In order to increase the flux of homogeneous PAN membranes, the thickness has been varied between 3 and 100 μm. These membranes have been tested for the dehydration of ethanol/water mixtures at a feed concentration of 90 w% ethanol, at 70°C.

In figure 4.2 the total flux and the pervaporation selectivity α^P are represented, as a function of the membrane thickness d. As expected, the flux increases with decreasing membrane thickness. The selectivity of the thick membranes is extremely high: values higher than $\alpha^P=10^4$ have been found. This means that the permeate contains only a very small amount of ethanol: less than 0.1 w% ethanol. The selectivity is rather constant for membrane thicknesses between 40 and 100 μm. For membranes with a thickness less than about 40 μm the selectivity decreases, especially below 10 μm. The thinnest membranes that could be prepared ($d\approx3$ μm) showed only a selectivity of about $\alpha^P=5$.

These results indicate that with the preparation method mentioned (evaporation of solvent) it was impossible to prepare thin PAN membranes that show both high flux and high selectivity. For commercial purposes only PAN membranes with thicknesses below 5 μm (fluxes $J>0.1$ kg/m^{2}h) and selectivities of at least $\alpha^P=1000$ would be of interest.

The results presented are not in agreement with the solution-diffusion model, which predicts a linear relation between the reciprocal flux and the membrane thickness, and a selectivity that does not depend on the thickness. There are several possibilities why the selectivity of a membrane decreases with decreasing membrane thickness (see also the review in chapter 1): artefacts in the membranes, membrane morphology, non steady-state experiments, sorption resistance, concentration polarization and temperature effects. In the paragraphs to follow these aspects will be investigated in relation to the results with the homogeneous PAN membranes.

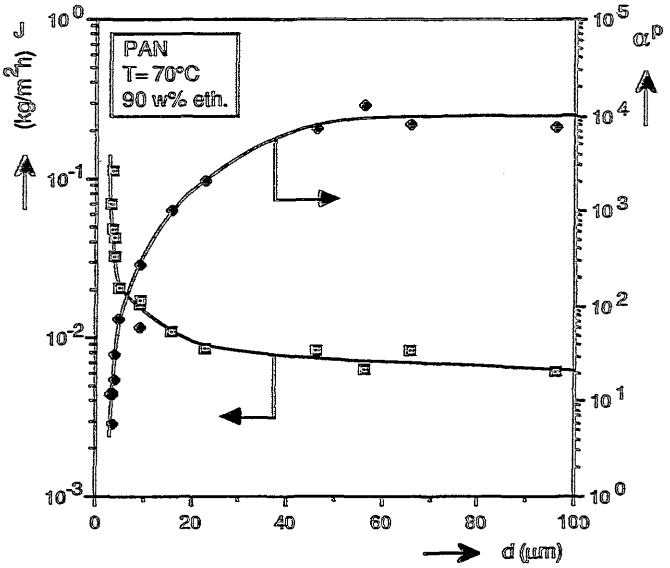

Figure 4.2: Flux J and selectivity α^P for homogeneous PAN membranes, as a function of the membrane thickness d.

In order to discuss these possible effects in relation to the solution-diffusion model more conveniently, the results of figure 4.2 are replotted in a different way in figure 4.3: here the reciprocal component fluxes of water $1/J_w$ and ethanol $1/J_e$ are given as a function of the membrane thickness. These reciprocal component fluxes represent the resistances of the membrane against transport of the components. In this figure also the expected component fluxes (represented by the dashed lines) are plotted. These expected component fluxes are calculated on the basis of the highest experimentally obtained selectivity, which is assumed to be the intrinsic (i.e. expected) selectivity, and taken to be operative over the full range of thicknesses. For a fixed feed concentration, the intrinsic selectivity determines the ratio of the expected component fluxes of water and ethanol:

$$\alpha^P = (c_w^P/c_e^P)/(c_w^f/c_e^f) = (J_w/J_e)/(c_w^f/c_e^f) \qquad (3)$$

The highest selectivity found was about α^P=10000. For a feed of 90 w% ethanol the expected ratio of the component fluxes J_w/J_e=10000∗(0.1/0.9)=1111, for all membrane thicknesses. The line for the expected component flux of ethanol J_e was plotted first, with the maximum slope on the basis of the experimental component fluxes of ethanol, in order to get acceptable expected component fluxes of water with J_w/J_e=1111.

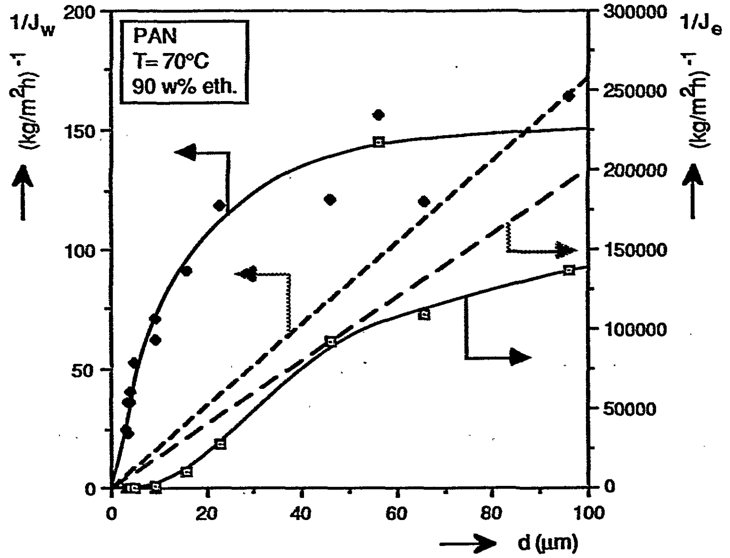

Figure 4.3: Reciprocal component fluxes of water $1/J_w$ and ethanol $1/J_e$ for homogeneous PAN membranes, as a function of the membrane thickness d.
Points and full lines: experimental values; dashed lines: expected curves (see text).

Figure 4.3 shows that for most membranes the component fluxes of water are smaller than expected (reciprocal component fluxes of water higher than expected). The experimental component fluxes of ethanol are for most membranes higher than expected.

The differences between the experimental and expected component fluxes should be explained by some other effects, which will be discussed in the following paragraphs.

Artefacts

Small artefacts originating from membrane preparation (like thin spots, dust particles, air bubbles, contaminants in the polymer or small cracks in the membrane) will have a stronger effect on membrane performance for thin membranes, than for thicker membranes. Because of these artefacts the fluxes (both component fluxes as well as total fluxes) through thin membranes generally will be higher than expected, and the selectivity will be lower than the intrinsic selectivity. In our experiments the experimental selectivity indeed is decreasing with membrane thickness, and also the component flux of ethanol for thin membranes is higher than expected. The experimental component fluxes of water are much smaller than expected, which is not in agreement with this suggested explanation.

Hence, the decrease in selectivity with decreasing membrane thickness can partly be explained by artefacts, due to the increased component flux of ethanol for thin membranes. Because the component fluxes of water for thin membranes are smaller than expected (which is in contradiction with the explanation of artefacts), there should be other factors to explain all detailed flux data. Furthermore, artefacts generally lead to non-reproducible results, whereas both our flux and selectivity results show a behaviour without scatter.

Membrane morphology

The homogeneous membranes were prepared by casting a solution on a glass plate, followed by evaporation of the solvent. The evaporation time was shorter for the thin membranes than for the thicker ones, which could have resulted in a different morphology of the ultimate membranes. To explore whether the morphology was dependent on membrane thickness, the following experiments have been performed.

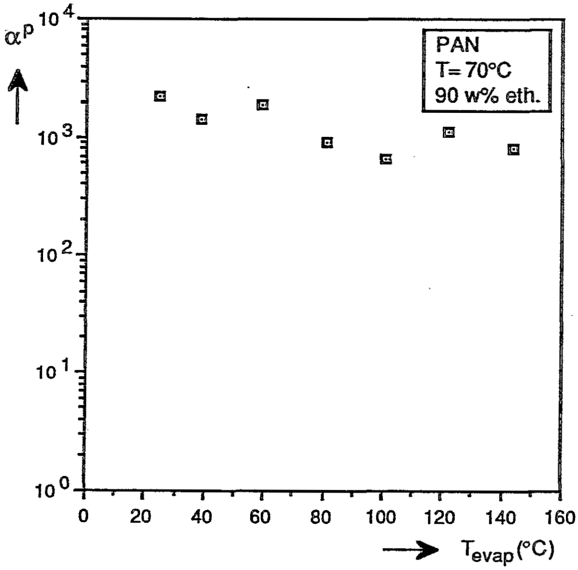

Figure 4.4: Selectivity α^P for homogeneous PAN membranes, as a function of the evaporation temperature of the solvent. Membrane thickness: 38-43 μm.

In the first series the temperature during evaporation of the casted polymer solutions has been varied. The pervaporation results of these membranes are given in figure 4.4. This figure shows that the selectivity generally decreases with increasing evaporation temperature. This effect of increased evaporation temperature can be compared to the faster evaporation of thinner casted polymer films. The fluxes of the membranes were not significantly influenced by the evaporation temperature. Although these experiments show the expected trend, the decrease in selectivity is not strong enough to bridge the gap in selectivities found for the thin membranes in figure 4.2.

In the second set of experiments multi-layer membranes have been tested during pervaporation, and the results are compared with the results of single-layer membranes with the same total thickness. Thin homogeneous membranes with a thickness of about 3-4 μm were used, and 1, 2, 3 or 4 membranes were stacked in the cell. In figure 4.5 the selectivities for these multi-layer membranes are plotted as a function of the (total) membrane thickness. Single-layer membrane selectivities at various thicknesses (taken from figure 4.2) are replotted in the same figure 4.5.

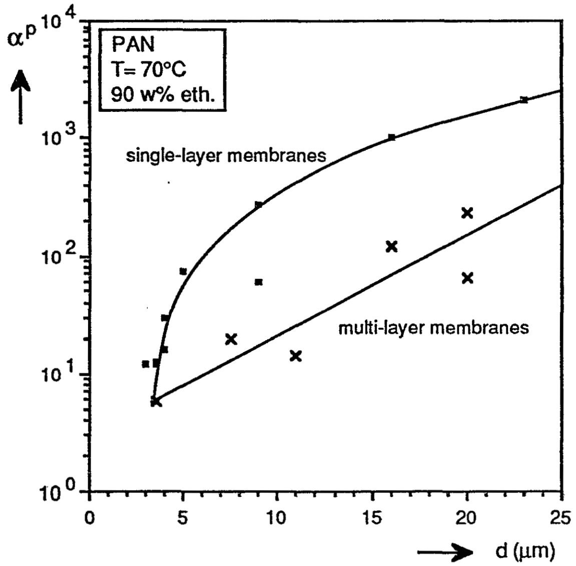

Figure 4.5: Comparison between selectivity α^P for single-layer membranes and for multi-layer membranes (1, 2, 3 and 4 layers) of PAN.

The figure shows that the selectivities for the multi-layer membranes are smaller (roughly by a factor of 10) than the selectivities of single-layer membranes with the same total thickness. The fluxes for the multi-layer membranes (not plotted in the figures) were proportional to the reciprocal thickness, and were somewhat higher than the fluxes for the single-layer membranes. Both the smaller selectivities and the higher fluxes for the multi-layer membranes are an indication that the morphology of the thin membranes differ considerably from those of the thick membranes. But, also for the multi-layer membranes the selectivity increases with increasing (total) thickness of the membranes. This slight increase of selectivity can be due to the fact that small artefacts in thin membranes generally will be covered by an imperfect-free part of an adjacent membrane in a multi-layer membrane. Hence, morphology can play an important role in the properties of homogeneous membranes.

Finally, membranes have been prepared, in which case the evaporation of the solvent (DMF) was carried out in a mixture of nitrogen gas and DMF vapour, instead of pure nitrogen gas. Because of a smaller driving force for evaporation of the solvent, the evaporation rate was smaller in that case. These membranes were also tested at the same feed conditions: 90 w% ethanol, at 70°C. The selectivities of the membranes are given in figure 4.6, together with the results of the membranes using pure nitrogen gas (replotted from figure 4.2).

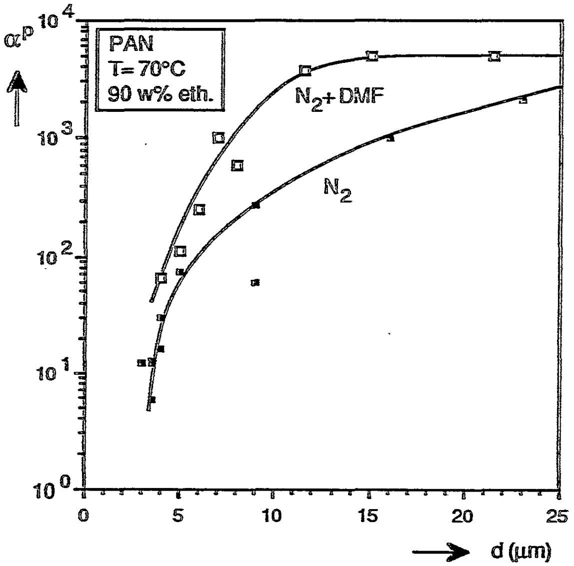

Figure 4.6: Selectivity α^P for homogeneous PAN membranes, as a function of the membrane thickness d, evaporated in nitrogen gas and in a mixture of nitrogen gas and DMF.

This figure shows that at the same membrane thickness higher selectivities are found for the membranes that were prepared using DMF in the nitrogen gas. The total fluxes (not given in the figure) are not influenced by the evaporation method. In figure 4.7 the selectivities for both types of membranes are plotted as a function of the flux. It is clear that with this preparation method higher fluxes can be obtained without loss of selectivity.

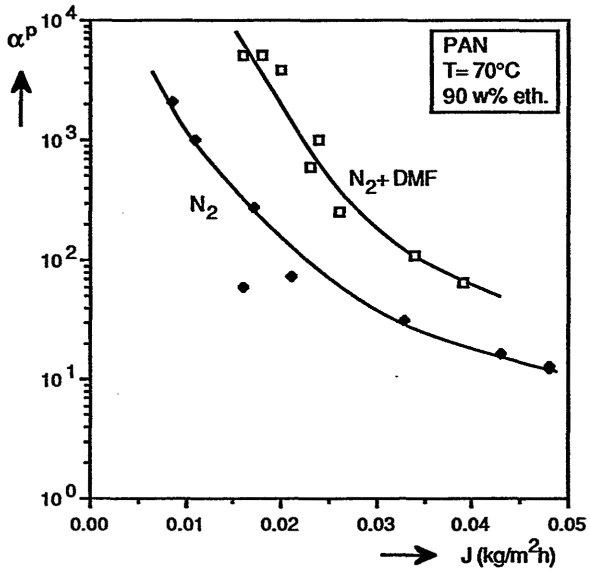

Figure 4.7: Comparison of flux J and selectivity α^P for homogeneous PAN membranes, evaporated in nitrogen gas and in a mixture of nitrogen gas and DMF.

From these three types of experiments it is concluded that the decrease in selectivity with decreasing membrane thickness can partly be explained by a difference in membrane structure of the thin membranes compared to that of the thick ones. The total fluxes were generally not strongly influenced by the membrane preparation method. This can be explained by the influence of the evaporation rate of the solvent on the membrane morphology. In a later stage of the evaporation process the flexibility of the polymer chains will decrease, and the chains will arrange into a final structure that is dependent on the evaporation rate. At higher evaporation rates the chains have less possibilities to arrange into the most dense structure. In our experiments a more dense membrane structure generally resulted in a higher selectivity, whereas the total fluxes were not changed significantly, or decreased only to a small extent. This means that the component flux of water is hardly influenced by the structure, whereas the component flux of ethanol decreases for a more dense structure. This can be explained by the fact that the larger molecule ethanol is hindered more by a more dense structure than water.

Thus, this influence of evaporation rate of the solvent on the membrane structure can explain the higher component fluxes of ethanol for thin membranes (leading to lower selectivities), but it can not explain the (relatively) low component fluxes of water for thin membranes. Hence, morphology effects can not explain all experimental results in detail.

Non-steady-state experiments

As mentioned in chapter 1, non-steady-state measurements can only have an effect on the flux and selectivity for thick membranes. Depending on the pre-treatment of the membranes, the fluxes through thick membranes can be higher or lower than expected from experiments with thinner membranes (where the steady-state is reached earlier), due to the build-up of a concentration-profile in the membrane. In our experiments the membranes were always pre-swollen in the feed mixture (at 20°C), meaning that the fluxes of the thick membranes are too high when the steady-state was not yet reached (the membrane has to deswell at the permeate side). This is in agreement with other experiments with PAN membranes performed in our laboratory, which showed that flux and selectivity are time dependent. In figure 4.8a the component fluxes of water and ethanol are given as a function of the pervaporation time (feed: 90 w% ethanol, 70°C).

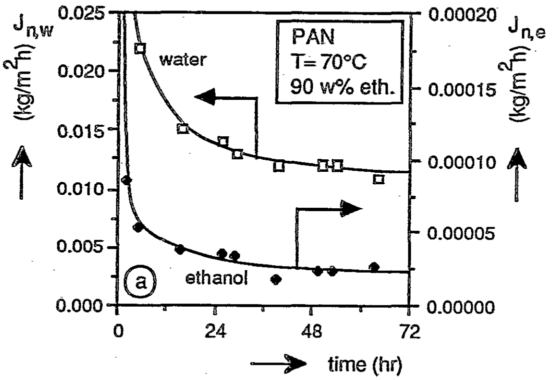

Figure 4.8a: Normalized component fluxes of water $J_{n,w}$ and ethanol $J_{n,e}$ for a homogeneous PAN membrane, as a function of pervaporation time. Membrane thickness: 18 μm.

This figure shows that both the component flux of water and of ethanol are decreasing with time, and reach a stationary state only after about 3 days. This decrease in flux must be due to relaxation phenomena in the polymer (membrane). Because the flux decrease is roughly the same (relatively) for both components, the selectivity is already constant after about 6 hours of pervaporation time, as can be seen from figure 4.8b.

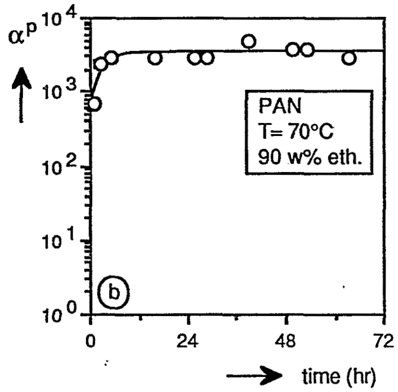

Figure 4.8b: Selectivity α^P for a homogeneous PAN membrane, as a function of pervaporation time. Membrane thickness: 18 μm.

Thus, if the steady-state has not yet been reached in thick membranes, the component fluxes of both water and of ethanol will be too high. This can explain the results in figure 4.3, where the component fluxes of ethanol of thick membranes are indeed higher than expected (on the basis of the fluxes of the thin membranes).

Sorption resistance

A sorption resistance (see chapter 1) can be defined when diffusion through the membrane is not the only rate-determining step of the transport mechanism (sorption-diffusion-desorption). This sorption resistance will become more apparent with decreasing membrane thickness. It will lead to smaller fluxes (total flux and component fluxes) for thin membranes. The selectivity can be higher or lower compared to thick membranes, because sorption resistances can be different for both components. Because in our experiments the component fluxes of ethanol are higher than expected, there is apparently no sorption resistance for transport of ethanol. But, because the component fluxes of water are smaller than expected, this is an indication for a sorption resistance for water transport.

Concentration polarization

Concentration polarization in pervaporation will always lead to lower (total) fluxes and lower selectivities (see chapter 6). Because all experiments were performed under the same conditions (concentration, temperature and stirring speed), differences in concentration polarization can only originate from differences in fluxes. Because fluxes for thin membranes are higher than for thick membranes, this will lead to a stronger decrease of fluxes and selectivities for thin membranes, which is in agreement with our experiments (figure 4.3). The extent of concentration polarization can be calculated if the mass transfer coefficient is known. For our experiments we used stirred cells, and unfortunately no appropriate equations are reported in literature to calculate mass transfer coefficients in stirred cells that provide corrections for non-ideal stirring conditions. In our case the mechanical stirrer was not positioned close enough to the membrane surface, and the stirrer dimensions were too small to utilize the best available equation reported in literature [4.20].

Because the effect of concentration polarization can explain our experimental results qualitatively, apparent mass transfer coefficients were calculated that are needed to get a good agreement between experimental and expected pervaporation results. Hereby it was assumed that concentration polarization is the only factor responsible for the deviations from the expected fluxes.

The calculations were performed using equation (4), which is derived in chapter 6 of this thesis. For the calculations we assumed an intrinsic selectivity of $\alpha^p=10^4$, from which the concentrations of the components at the membrane wall were calculated (the intrinsic selectivity is related to the actual wall concentrations and the actual permeate concentrations).

$$J^m/(k.\rho^p) = \ln\{(\rho^w c_2^w - \rho^p c_2^p)/(\rho^b c_2^b - \rho^p c_2^p)\} \qquad (4)$$

By substitution of the experimental fluxes (J^m), bulk and permeate concentrations, and the densities of the feed, the permeate and the liquid at the membrane wall, apparent mass transfer coefficients were determined for each experiment. These calculations showed that all experimental results (both component fluxes and selectivity) could be described properly with an apparent mass transfer coefficient of about $k \approx 10^{-7}$ m/s.

However, the value of $k=10^{-7}$ m/s is probably much smaller than the actual value of k in the cells during our experiments. Approximate calculations using mass transfer relations from literature ([4.20]) for our cell dimensions, using ideal stirrer position and dimensions, resulted in a value for k that must be higher by a factor of approximately 250-400.

Temperature effects

Flux and selectivity during pervaporation can be influenced by two temperature effects. During the transport of the components through the membrane a phase transition takes place. The necessary heat of evaporation is generally supplied by the feed. The transfer of heat towards the membrane leads to a temperature drop near the membrane wall at the feed side. This first effect is called temperature polarization. Secondly, due to this phase transition taking place over the membrane (liquid → vapour) a temperature drop will be established over the membrane. Both effects increase with increasing flux through the membrane, which is the case for thinner membranes. These effects lead to a decrease of the average temperature in the membrane, at which the actual flux and selectivity are determined. This lower temperature generally leads to lower fluxes; the selectivity can both increase and decrease due to this temperature drop.

Because in our experiments the fluxes were relatively small, it is likely that these temperature effects will be negligible, and have not influenced our experimental results.

4.3.2 Influence of the feed conditions on flux and selectivity

Feed temperature

Another way to increase fluxes through membranes, is to increase the temperature of the feed, since diffusion coefficients generally increase strongly with temperature. In figure 4.9a the pervaporation flux is given as a function of the feed temperature at a feed concentration of 90 w% ethanol (all experiments were performed with a single membrane sample).

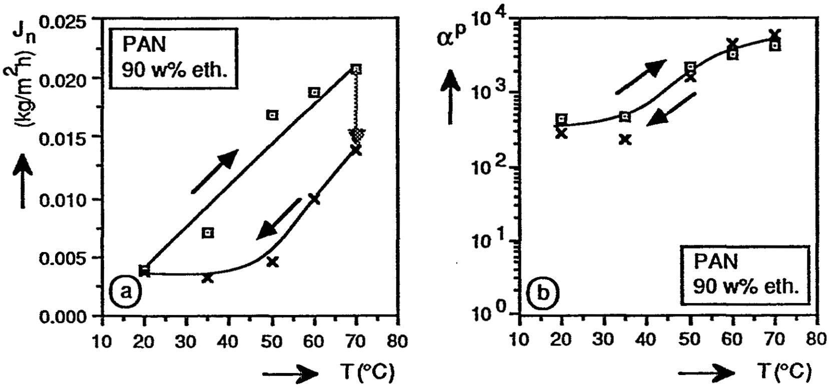

Figure 4.9: Normalized flux J_n (a) and selectivity α^P (b) for a homogeneous PAN membrane, as a function of the feed temperature. Membrane thickness: 23 µm.

First the temperature was increased from 20°C to 70°C (in a sequence of one temperature step each day), and then the same procedure was repeated from 70°C to 20°C.

The figure shows that with increasing feed temperature the total flux increases strongly, as expected. After the experiments at 70°C the membrane remained two more days at that temperature, and the flux and selectivity were determined again. The flux had decreased by about 30% during these three days, as indicated by the arrow in the figure. This flux decrease must be due to relaxation phenomena, which proceeds rapidly at higher temperatures, as was seen before in figure 4.8a. When the temperature was decreased from 70°C to 20°C, the fluxes decreased. When the temperature was maintained at 20°C for two more days, the flux decreased further (about 50%), but upon increasing the temperature again the same flux was found at 70°C as during the first cycle.

The selectivity (figure 4.9b) also increased with increasing temperature during the temperature cycle, which is rather uncommon for pervaporation using glassy polymer membranes. So in this case the optimal membrane properties (both for flux and selectivity) are obtained at the highest temperature possible. The selectivity did not show the hysteresis as was found for the flux. The selectivity was not influenced by the temperature history of the membrane: at decreasing temperature the same selectivity was found compared to increasing temperature. This is due to the fact that both component fluxes of water and ethanol were influenced to the same extent as a result of the temperature variation.

Concentration polarization

Although concentration polarization actually is an effect mainly determined by the (process) feed conditions, the effect of concentration polarization on our results has already been discussed in the previous paragraph. In our case concentration polarization was only influenced by the flux through the membrane, which is dependent on the membrane thickness.

Feed composition

The feed composition is of great importance for practical applications. Generally in practice this parameter is a constant factor, which can not be chosen freely to influence the pervaporation properties. If a polymer has been selected as a membrane material on the basis of experiments at one single feed concentration because of excellent flux and selectivity, it should be kept in mind that in membrane modules the actual composition of the feed will change due to preferential permeation of one component from the feed mixture. So, polymers should be selected on the basis of a great number of experiments, covering the whole possible range of feed conditions that are of practical interest.

In figure 4.10 the flux and the selectivity are presented as a function of the ethanol content in the feed (at 70°C), using the same membrane for all experiments.

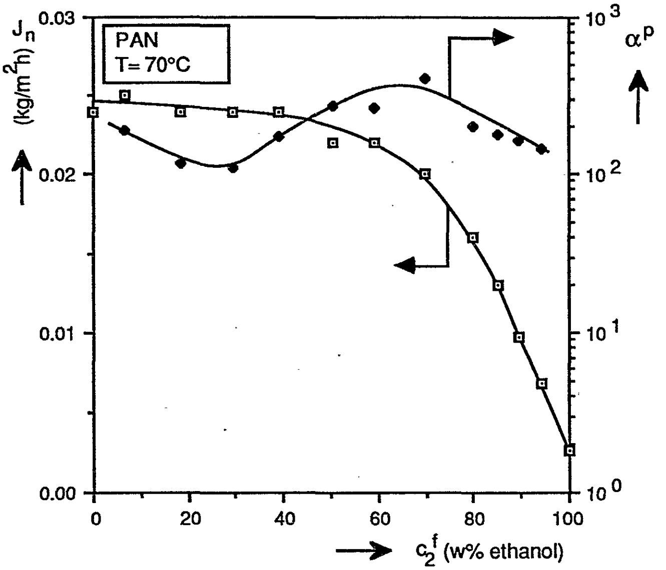

Figure 4.10: Normalized flux J_n and selectivity α^P for a homogeneous PAN membrane, as a function of the feed composition. Membrane thickness: 22 µm.

At low ethanol concentration the flux is constant, for higher concentrations (>50 w% ethanol) the flux decreases strongly, due to the decrease of total sorption of the mixture in the membrane with increasing ethanol concentration (as reported by Mulder et al [4.1] for sorption at 20°C). The selectivity is also dependent on the feed concentration and varies between about α^P=100 and α^P=400. Even at low ethanol concentrations in the feed the selectivity is still very high, which is rather surprising for pervaporation. Usually the selectivity decreases for increasing concentration of the preferentially permeating component in the feed, because the swelling of the polymer increases in the same direction. In this case the selectivity remains high, because the swelling of PAN in ethanol/water mixtures is very small (at 25°C the equilibrium uptake of ethanol/water mixtures, for any feed concentration, is less than 9 w% [4.1]).

It should be mentioned further that for industrial applications not only the effect of the feed composition and temperature should be considered, but also the effect of the permeate pressure. In laboratory scale experiments generally very low partial pressures of the permeating components can be created (e.g. by using liquid nitrogen temperatures), resulting in maximal flux and selectivity values. Under practical conditions the permeate usually is condensed with cold water, generally resulting in lower fluxes and selectivities.

4.4 Conclusions

Homogeneous PAN membranes show extremely high selectivities for the dehydration of ethanol/water mixtures by pervaporation. For a feed mixture of 90 w% ethanol at 70°C the selectivity for thick membranes is about $\alpha^P=10^4$, which means that the permeate contains less than 0.1 w% ethanol. The (low) fluxes of these highly selective membranes could be increased by decreasing the membrane thickness, but only at the expense of the selectivity (especially for membranes with thicknesses less than 10 μm). This decrease in selectivity has been investigated further by comparing the experimental component fluxes (as a function of the membrane thickness) with the expected component fluxes (from the solution-diffusion model and the intrinsic selectivity). The decrease in selectivity for extremely thin membranes (d<5μm) must partly be contributed to small artefacts in the membranes. This can probably be avoided by filtering the polymer solution before casting, and evaporation of the solvent in a clean environment.

The main factor determining the properties of the thinner membranes is the membrane morphology. The morphology of a polymer membrane can be influenced in two ways. The first way is by changing the membrane preparation method. The most important factor is the evaporation rate of the solvent. With decreasing evaporation rate (or increasing evaporation time) the pervaporation selectivity was increased: this was demonstrated by using multi-layer membranes, by the influence of the evaporation temperature and by the effect of evaporation in a solvent-containing atmosphere. The membrane morphology is also changed during the pervaporation experiments, due to relaxation of the polymer. Relaxation phenomena lead to a decrease of component fluxes in time of both water and ethanol, whereas the selectivity remains constant.

An important overall conclusion is that the selectivity of homogeneous membranes can be influenced strongly by the preparation method; higher selectivities can be obtained if the evaporation rate of the solvent is decreased. This can be achieved either by evaporation at a lower temperature or by evaporation in a solvent-containing environment, but also by the choice of a solvent (less volatile).

In spite of the fact that thin homogeneous PAN membranes can be prepared now with higher fluxes at the same selectivity, and an increase of both flux and selectivity with increasing temperature is observed, the fluxes of the membranes are still rather small; relaxation phenomena further decrease these low fluxes.

4.5 List of symbols

c_i = weight fraction of component i in the liquid (feed, permeate, membrane wall) (g/g)
d = membrane thickness (μm)
D_i = diffusion coefficient of component i in the membrane (m^2/h)
J = total pervaporation flux (kg/m^2h)
J_i = pervaporation flux of component i (kg/m^2h)
J_n = total pervaporation flux, normalized to 10 μm membrane thickness (kg/m^2h)
k = mass transfer coefficient (m/s)
M_w = weight averaged molecular weight of the polymer (Dalton)

α^p = pervaporation selectivity (-)
ρ = density (feed, permeate, membrane wall) (kg/m^3)

subscripts
e = ethanol, less permeable component
w = water, preferentially permeating component

superscripts
b = bulk feed
f = feed
m = membrane, mass
p = permeate, pervaporation
w = membrane wall at the feed side

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Chapter 5

Pervaporation of ethanol/water mixtures using homogeneous blend membranes.

J.W.F. Spitzen, M.H.V. Mulder, C.A. Smolders

Summary

Homogeneous membranes were prepared by blending poly(acrylonitrile) (PAN) or poly(sulfone) (PSf) with the water-soluble polymers poly(vinylpyrrolidone) (PVP) or poly(maleicanhydride) (PMA). Blend membranes prepared with different compositions of PAN/PVP, PAN/PMA and PSf/PVP were used to dehydrate ethanol/water mixtures by pervaporation. The flux and selectivity were determined as a function of the blend composition, and for two blends as a function of the feed concentration. For all blends the fluxes increased by adding the water-soluble polymers, but the selectivity decreased. The influence of sorption on the separation mechanism was investigated by total and preferential sorption experiments for the PAN/PVP blend.

5.1 Introduction

The aim of most membrane material research is to develop membranes that combine a high transport rate through the membranes with high separation characteristics. Because usually high fluxes are accompanied by low selectivities and vice versa, membrane development is often characterized by an optimization procedure.

Since for pervaporation processes generally the fluxes can be increased by increasing the temperature of the feed or by decreasing the effective thickness of the membrane, usually the optimization towards a high selectivity has the first priority. The selectivity of membranes is mainly determined by the choice of the polymer material. Starting point of new developments for a given separation problem is then the selection of a very selective polymer. For the dehydration of ethanol/water mixtures membranes of poly(acrylonitrile) (PAN) and poly(sulfone) (PSf) are known to be very selective (see chapter 4 and [5.1]): the permeability of ethanol is extremely low compared to the permeability of water. But also the total permeability of these membranes is very low, due to the low diffusion rates and the low affinity of the polymers towards ethanol/water mixtures (the sorption of these mixtures in PAN and PSf is only a few percent [5.2]). This affinity towards aqueous liquid mixtures can be increased by several methods, e.g. by:

a) grafting of a hydrophilic polymer or introduction of specific functional groups on the selective polymer's backbone (this can also be directly performed on the ready membrane),
b) using a copolymer of the selective polymer and a hydrophilic polymer [5.3-5.7], or
c) blending of the selective polymer with a hydrophilic polymer.

Grafting is a rather complicated technique, which is difficult to perform on a large scale. The use of copolymers also has some disadvantages: there exists only a small number of copolymers of PAN or PSf, and usually they are very expensive. A more gentle way to influence the hydrophilicity of a polymer membrane is to use polymer blends.

In this chapter results are presented on the dehydration of ethanol/water mixtures by pervaporation, using various blend membranes. PAN and PSf were chosen as the selective components in the blends. Both polymers were blended with poly(vinylpyrrolidone) (PVP), because PVP is a hydrophilic polymer and it is known from literature that homogeneous PSf/PVP [5.8] and PAN/PVP [5.9] blends can be prepared. Also blend membranes were prepared of PAN with another hydrophilic polymer, poly(maleicanhydride) (PMA), and the results were compared with those of a copolymer of PAN and PMA, which was also available. Equilibrium sorption experiments (total sorption and preferential sorption) have been performed with the blends PAN/PVP. By comparing the results of the sorption and the pervaporation experiments, the influence of sorption on the total separation mechanism was investigated.

5.2 Theory

The aim of polymer blending usually is to create a new polymeric material that should combine the properties of two (or more) homopolymers. Most research concerning polymer blending has been focussed on improvement of the mechanical properties of polymer materials, in relation to their processability (influencing e.g. the glass transition temperature, melting temperature, tensile modulus or impact strength). Generally blends are made of two polymers that have rather unique but opposite properties, and the aim of blending is that the desired properties of both homopolymers are combined in the blend material.

Two types of polymer blends can be distinguished: homogeneous blends and heterogeneous blends. In homogeneous blends two (or more) polymers are mixed on a molecular level. In that case generally the properties of the two polymers are additive, leading to a more or less linear relation between a special property and the composition of the blend. In some special cases the properties of the homogeneous blend can be superior compared to the properties of both pure homopolymers. This *synergistic effect* is possible if some specific interactions between the two polymer molecules are possible.

In heterogeneous blends (micro-)domains of one polymer in the other polymer phase are present. Although the mechanical properties of such heterogeneous blend might still be improved (compared to the two homopolymers), the chemical and physical properties usually are not improved. Mostly a sigmodial relationship is found for the dependence of a property of the heterogeneous blend on the composition. In some cases a property can show a minimum as a function of the blend composition.

The main advantage of using blends is that the chemical, physical and mechanical properties can be influenced by changing the composition of the blend; this means that the properties can be optimized easily. Another advantage could be that the method of blending is generally relatively simple. The main problem in polymer blending is to find two polymers that first have the desired properties, and second are compatible.

For the development of blend membranes that show improved separation properties in comparison to the homopolymer membranes, homogeneous blends are needed. In general, the miscibility of polymers is very poor. From a thermodynamic point of view, two polymers can mix at a molecular level, if the free energy of mixing ΔG_m is negative:

$$\Delta G_m = \Delta H_m - T.\Delta S_m < 0 \qquad (1)$$

The entropy of mixing ΔS_m for macromolecular compounds is extremely small. Hence, the contribution of $-T\Delta S_m$ to ΔG_m is negligible. This implies that generally ΔG_m can only be negative if ΔH_m is negative. If only dispersive or Van der Waals interactions between the two polymers are possible, ΔH_m is always positive, as can be concluded from equation (2):

$$\Delta H_m = V.(\delta_1 - \delta_2)^2.\phi_1\phi_2 \qquad (2)$$

This equation shows that only for two polymers with (almost) equal solubility parameters δ_1 and δ_2, ΔH_m could be small enough to make ΔG_m negative.

If specific interactions between the polymer segments take place (e.g. dipole-dipole interactions, electron donor-acceptor interactions or hydrogen bonding) a negative, exothermic term ΔH^*_m is added to ΔH_m, possibly leading to an overall negative H'_m:

$$\Delta H'_m = V.(\delta_1 - \delta_2)^2.\phi_1\phi_2 + \Delta H^*_m \qquad (2a)$$

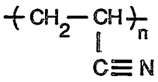
Thus, specific interactions favour the formation of homogeneous blends.

Already a lot of work has been reported on the use of polymer blends for membrane development, and a short survey was reported by Lloyd et al [5.10]. Also for pervaporation blend membranes have been used; an overview is given in table 5.1. Recently Nguyen [5.11] reported on a great number of pervaporation experiments using polymer blend membranes (mostly of water soluble polymers) for the dehydration of ethanol/water mixtures.

Table 5.1: Examples of the use of polymer blends for pervaporation membranes.

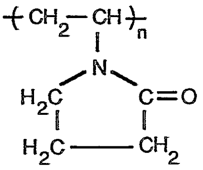
polymer 1	polymer 2	liquid mixture	reference
Poly(acrylonitrile)	Poly(vinylpyrrolidone)	water/organic liquids	[5.9]
Carboxymethylcellulose	Poly(acrylic acid)-Na^+	water/alcohols	[5.11]
Carboxymethylcellulose	Poly(vinylsulfonic acid)-Na^+	water/ethanol	[5.13]
Nylon-6	Poly(acrylic acid)	water/ethanol, acetic acid	[5.14]
Poly(vinylalcohol)	Poly(hydroxycarboxylic acid)	water/acetic acid	[5.15]
Poly(vinylalcohol)	Poly(vinylpyrrolidone)	water/acetic acid	[5.15]
Poly(vinylalcohol)	Poly(acrylic acid)	water/acetic acid	[5.15]
Acetylcellulose	Poly(phosphonates)	benzene/cyclohexane	[5.16]
Poly(phosphonates)	Cellulose acetate	organic liquid mixtures	[5.17]
Poly(phosphate)	Cellulose acetate	organic liquid mixtures	[5.17]
Poly(vinylalcohol)	Poly(ethylene glycol)	water/ethanol	[5.18]

The structural formulas of the polymers used in this chapter are given below.

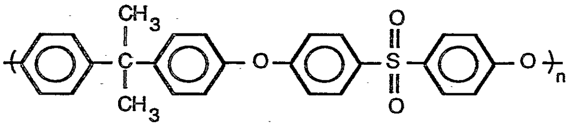


$$-\!\!\left(CH_2-\underset{\displaystyle C\equiv N}{\underset{|}{CH}}\right)_{\!n}\!-$$

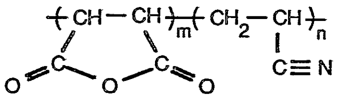
Poly(acrylonitrile)



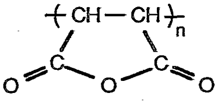
Poly(vinylpyrrolidone)



Poly(sulfone)



Poly(acrylonitrile maleicanhydride)



Poly(maleicanhydride)

Some physical and chemical properties of these polymers are listed in table 5.2.

Table 5.2: Physical and chemical properties of the polymers used, and of ethanol and water, at 25°C.

	ρ (g/cm^3)	M_u (g/mole)	δ (cal/cm^3)$^{1/2}$	V_i (cm^3/mole)
PAN	1.17	53.1	12.5	45.4
PSf	1.22	442.5	10.5	362.7
PVP	1.20	111.1	12.6	92.6
PMA	-	98.1	-	-
water	0.997	18.0	23.5	18.1
ethanol	0.785	46.1	12.9	58.7

PAN and PSf were chosen because homogeneous membranes of these polymers have high pervaporation selectivities for the dehydration of ethanol/water mixtures. The hydrophilic polymer PVP was chosen to increase the fluxes of the PAN and PSf membranes, because it was known from literature that homogeneous blends of PAN/PVP [5.9] and PSf/PVP [5.8] can be prepared. From table 5.2 it can be seen that the solubility parameters of PAN and PVP are about the same, which is an indication for the ease of formation of a homogeneous blend.

5.3 Experimental

5.3.1 Materials

Poly(acrylonitrile) was obtained from Du Pont (PAN-A; M_w=516,000 Dalton), poly(vinylpyrrolidone) (PVP) from Janssen Chimica (M_w=360,000 Dalton), poly(sulfone) (PSf) from Union Carbide (P3500), and poly(maleicanhydride) (PMA) and poly(acrylonitrile-co-maleicanhydride) (P(AN-MA)) from Polysciences. Dimethylformamide (DMF) (reagent grade) and ethanol (analytical grade) were used without further purification; water was ultrafiltrated before use.

5.3.2 Membrane preparation

Casting solutions were prepared by dissolving both polymers constituting the blend in the solvent (DMF) at a total concentration of 20 w%. First PVP or PMA was dissolved, then PAN or PSf was added; a clear, homogeneous solution was obtained after heating the solution. Upon cooling the casting solution remained homogeneous (no visible phase separation). The compositions of the blends are denoted by the weight fraction X of the hydrophilic polymer (PVP or PMA) related to the total amount of polymer in the casting solution. Homogeneous membranes were prepared by casting the solution on a glass plate. The solvent was removed by evaporation in a nitrogen atmosphere at room temperature. In all cases completely transparent membranes were obtained.

5.3.3 Sorption experiments

Equilibrium sorption experiments were performed at 25°C, using thick strips (thickness of about 200 μm, dry weight of about 0.2 g.) of membranes of the PAN/PVP blend. The total sorption and the preferential sorption of a mixture of 50 w% ethanol in water in these blend membranes were determined, as a function of the composition of the blend. All experiments were performed in triplo, and the three results were averaged.

The experimental method is described in chapter 2 of this thesis. The total sorption is represented by Q: grams of absorbed liquid per gram dry polymer. The sorption results can also be presented by the component sorption data. From the total sorption Q and the composition of the absorbed liquid in the membrane the component sorption of water (Q_w) and ethanol (Q_e) is calculated: $Q_w=Q.c_w{}^m$ and $Q_e=Q.c_e{}^m$ (with $c_w{}^m+c_e{}^m=1$). By comparing the dry weight of the membranes before and after the sorption experiments, the weight loss due to solution of the PVP in any ethanol/water mixture could be determined.

The preferential sorption was determined with a different set of membranes. It is represented by the equilibrium sorption selectivity α^s, which is calculated from the liquid composition of the feed (f) and the composition of the absorbed liquid in the membrane (m), according to:

$$\alpha^s = (c_w{}^m/c_e{}^m)/(c_w{}^f/c_e{}^f) \qquad (3)$$

The composition of the liquids was determined by gas chromatography.

5.3.4 Pervaporation experiments

The pervaporation experiments were performed employing two stirred glass cells, as described by Mulder et al [5.12]. The effective membrane areas in the cells are 71 cm^2 and 80 cm^2. The pressure at the downstream side was kept below 500 Pa by a vacuum pump. The permeate was collected in cold traps, which were cooled by liquid nitrogen. Fluxes were determined every hour during eight hours by determination of the weight increase of the cold traps. Experiments were performed at two standard feed conditions: 50 w% ethanol in water at 25°C (to compare the pervaporation results with the equilibrium sorption experiments) and 90 w% ethanol in water at 70°C. The pervaporation properties are characterized by the flux J and the pervaporation selectivity α^p.

The fluxes of the different membranes were normalized to a membrane thickness of 10 μm, assuming a proportionality between the flux J and the reciprocal membrane thickness 1/d: $J_n=J.d/10$ (kg/m^2h).

The fluxes can also be presented by the component flux data. From the total flux J_n and the composition of the permeate, the component fluxes of water ($J_{n,w}$) and ethanol ($J_{n,e}$) are calculated: $J_{n,w}=J_n.c_w^p$, and $J_{n,e}=J_n.c_e^p$ (with $c_w^p+c_e^p=1$).

The pervaporation selectivity α^p was calculated from the liquid composition of the feed (f) and the permeate (p) according to equation (4). α^p is assumed to be independent of the membrane thickness within the range of thicknesses used.

$$\alpha^p = (c_w^p/c_e^p)/(c_w^f/c_e^f) \qquad (4)$$

The thickness of the dry membranes varied between 15 and 25 µm. The composition of the liquids was determined by gas chromatography.

5.4 Results and discussion

5.4.1 Sorption

PAN/PVP

The swelling of homogeneous membranes of PAN/PVP blends in a 50 w% ethanol/water mixture was determined at 25°C for different blend compositions. The results are presented in figure 5.1, where the total sorption Q is given as a function of the weight fraction of PVP in the blend. The figure clearly shows that more liquid is absorbed in the blend with increasing PVP content. At low PVP content (from 0-10 w% PVP) the swelling is constant: about 6.5 w%. At higher concentrations of PVP the swelling increases strongly, up to about 90 w% for X=0.50.

The results of preferential sorption experiments are presented in figure 5.2, where the equilibrium sorption selectivity α^s (defined by equation (3)) is plotted as a function of the composition of the blends. The figure shows that at low PVP content (0-5 w% PVP) the sorption selectivity α^s increases, and at higher PVP contents decreases again. The relatively low sorption selectivity for pure PAN is rather unexpected, because by extrapolating the results for the blends in the same figure, a very high sorption selectivity could be expected ($\alpha^s \approx 1000$). However, all three experiments for pure PAN gave smaller sorption selectivities than the experiments for the PAN/PVP blends with 5 w% PVP.

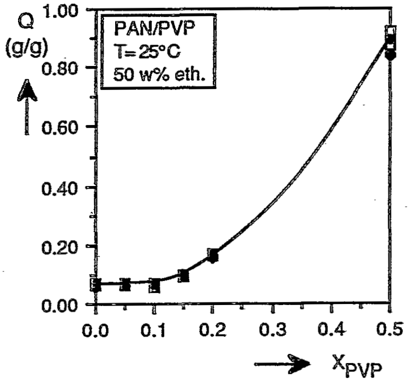


Figure 5.1: *Total sorption Q of a 50 w% ethanol/water mixture in PAN/PVP blends, as a function of the composition X of the blend (weight fraction PVP).*

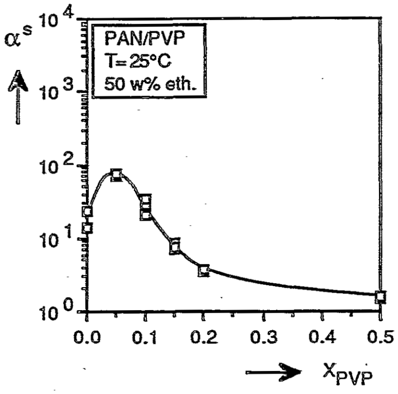


Figure 5.2: *Equilibrium sorption selectivity α^S of a 50 w% ethanol/water mixture in PAN/PVP blends, as a function of the composition X of the blend (weight fraction PVP).*

Because the total sorption Q (see figure 5.1) is constant from 0-10 w% PVP in the blend, the increase in sorption selectivity must be due to an increase of the interaction between the polymer (blend) and water, or due to a decreased interaction with ethanol. If the total sorption Q is divided into the component sorption of water Q_w and the component sorption of ethanol Q_e, it is clear (see figure 5.3) that the increase of α^s at low PVP content is due to a decrease of the component sorption of ethanol.

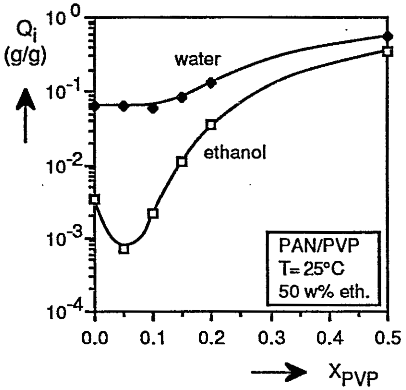


Figure 5.3: Component sorption Q_i of water and ethanol from a 50 w% ethanol/water mixture in PAN/PVP blends, as a function of the composition X of the blend (weight fraction PVP).

A possible explanation for this phenomenon is that at low PVP content water and ethanol have to compete with PVP with respect to interactions with PAN. In pure PAN the interaction between ethanol and PAN is much weaker than the interaction between water and PAN, leading to a preferential sorption of water. Due to the low overall sorption of ethanol/water mixtures in PAN also the difference in molar volumes of ethanol and water contributes to a large extent to the preferential sorption of water. When PVP is present, which can form hydrogen bonds too, a stronger interaction of PVP with PAN, competing with that of ethanol with PAN, may lead to a decreased sorption of ethanol in PAN. The interaction between PAN and water is not influenced, probably because the interaction between PAN and water is stronger than the interaction between PAN and PVP. However, it should be kept in mind that sorption of binary liquid mixtures in polymer blends is a complex phenomenon, where different interactions between the components have to be considered in a quaternary system.

At higher PVP contents both the component sorption of water Q_w and ethanol Q_e increase, leading to an increase of the total sorption, which, due to the plasticizing effect, results in a decrease of the sorption selectivity α^s.

5.4.2 Pervaporation

PAN/PVP

In figure 5.4 the pervaporation results of the PAN/PVP blend membranes are presented, as a function of the composition of the blend, at 25°C for 50 w% ethanol in water. The figure shows that by blending PAN and PVP the pervaporation characteristics (both flux and selectivity) can be influenced by a factor of about 500. By increasing the PVP content in the membrane, the pervaporation selectivity decreases from about $\alpha^P=650$ for pure PAN to about $\alpha^P=1.8$ for the blend with 15 w% PVP, whereas the flux increases from $J_n=0.012$ kg/m^{2}h for pure PAN to $J_n=5.6$ kg/m^{2}h for the blend with 50 w% PVP.

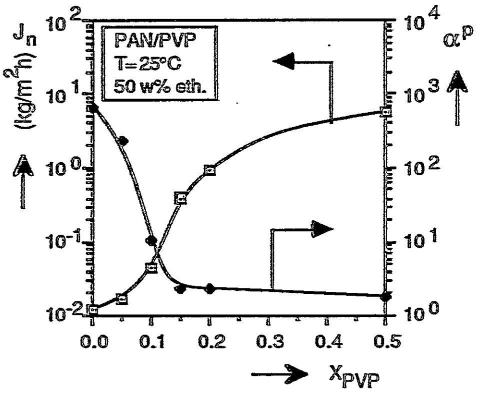


Figure 5.4: Normalized pervaporation flux J_n and selectivity α^P for a 50 w% ethanol/water mixture for PAN/PVP blend membranes, as a function of the composition X of the blend (weight fraction PVP).

In figure 5.5 the component fluxes of water and ethanol are given, as calculated from the total flux and the permeate composition. By increasing the PVP content the component fluxes of both water and ethanol increase. This can be explained by the fact that PVP is a polymer with strong interactions with ethanol and water (water and ethanol are solvents for PVP). Because in pure PAN the component flux of ethanol is extremely low, it is not surprising that the effect of PVP is stronger for the component flux of ethanol compared to that for water. This relatively stronger increase of the component flux of ethanol causes the decrease of the pervaporation selectivity. For X>0.15 the effect of PVP on the component fluxes of water and ethanol is about the same.

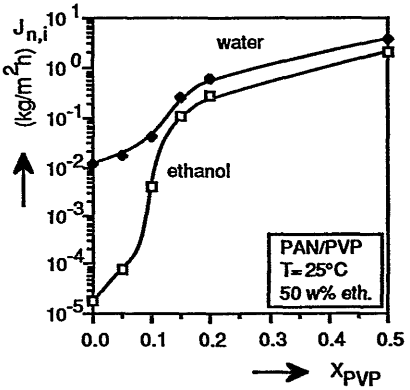


Figure 5.5: Normalized component fluxes $J_{n,i}$ of water and ethanol for a 50 w% ethanol/water mixture for PAN/PVP blend membranes, as a function of the composition X of the blend (weight fraction PVP).

The same general trend was found for a feed of 90 w% ethanol in water at 70°C (see figure 5.6), although both flux and selectivity are somewhat higher here compared to figure 5.4: by increasing the PVP content the total flux increases and the selectivity generally decreases. Only at low PVP content (X<0.05) both flux and selectivity do increase. Thus, addition of a small amount of PVP gives an overall improvement of the membrane properties. The increase of both

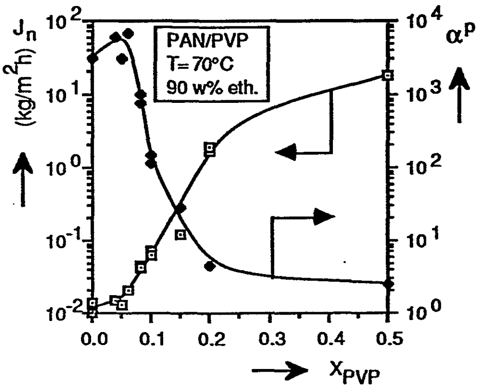


Figure 5.6: Normalized pervaporation flux J_n and selectivity α^P for a 90 w% ethanol/water mixture for PAN/PVP blend membranes, as a function of the composition X of the blend (weight fraction PVP).

flux and selectivity can be considered as a *synergistic effect*, which is rather exceptional in membrane development. From the figure it can be concluded that the optimal blend composition is around PAN/PVP=95/5. Although no sorption experiments are performed for these feed conditions, the synergistic effect at low PVP content can be due to a decrease of the component sorption of ethanol, which was found at 25°C and 50 w% ethanol in the feed (see figure 5.3).

At somewhat higher PVP content the pervaporation selectivity changes dramatically. Within the small range of blend compositions from X=0.06 to X=0.10 the selectivity drops from about 5000 to 130. At even higher PVP content the selectivity decreases further to about $\alpha^P=3$.

PSf/PVP

In figure 5.7 the pervaporation results are given for the PSf/PVP blend membranes, for 90 w% ethanol in water at 70°C. Unfortunately it was not possible to use pure PSf membranes at these high temperatures in 90 w% ethanol; after 1-2 hours pervaporation the membranes ruptured. Qualitatively the same trend was found as for the PAN/PVP blends: by increasing the content of PVP in the blend the flux increases and the pervaporation selectivity decreases. Compared to the PAN/PVP blends, the fluxes are higher and the selectivities are lower at the same (weight) content of PVP in the blend. This might be due to the more hydrophobic character of PSf compared to PAN: the sorption of ethanol/water mixtures at high ethanol content in PSf is higher than in PAN [5.2].

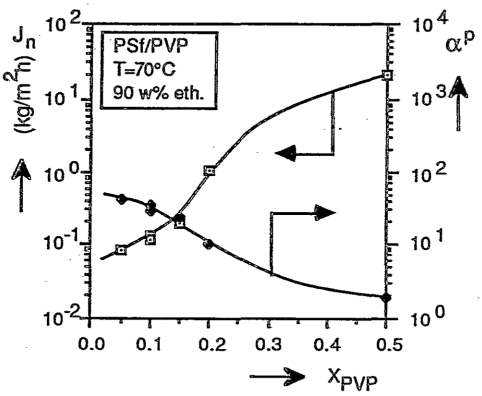


Figure 5.7: Normalized pervaporation flux J_n and selectivity α^P for a 90 w% ethanol/water mixture for PSf/PVP blend membranes, as a function of the composition X of the blend (weight fraction PVP).

PAN/PMA

In figure 5.8 the pervaporation results are presented for the PAN/PMA blend membranes, for 50 w% ethanol in water at 25°C. Again, addition of the hydrophilic polymer to the blend increases the flux during pervaporation and the pervaporation selectivity decreases. But, the effect of an equal amount of the hydrophilic polymer (by weight) is less pronounced compared to the influence of PVP for the blends PAN/PVP. Especially the selectivity does not decrease very much when the PMA content increases. The difference in dependence of the pervaporation properties on the content of hydrophilic polymer in the blends must be explained by differences in interactions between the hydrophilic polymer and the feed components. The higher fluxes for the PAN/PVP blends can also be due to the flexibility of the bulky pyrrolidone groups in PVP, compared to the more rigid anhydride groups in PMA.

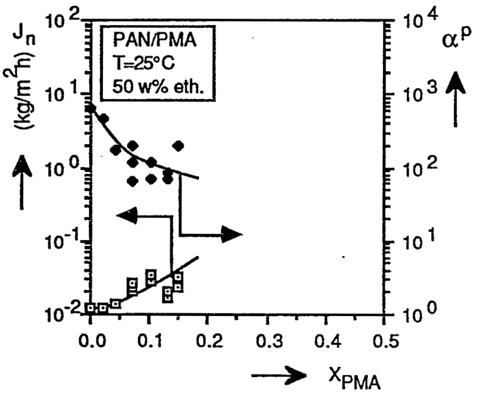


Figure 5.8: Normalized pervaporation flux J_n and selectivity α^P for a 50 w% ethanol/water mixture for PAN/PMA blend membranes, as a function of the composition X of the blend (weight fraction PMA).

In figure 5.9 the pervaporation results are given for the same membranes, but for a feed of 90 w% ethanol at 70°C. Again the results show the same trend as the PAN/PVP blends at the same feed conditions (figure 5.6), but comparable to the experiments at 25°C more PMA is needed (compared to PVP) to get the same effect on the flux or selectivity. Another resemblance with the PAN/PVP blend is the increase of both flux and selectivity at low content of the hydrophilic polymer, PMA in this case (synergistic effect).

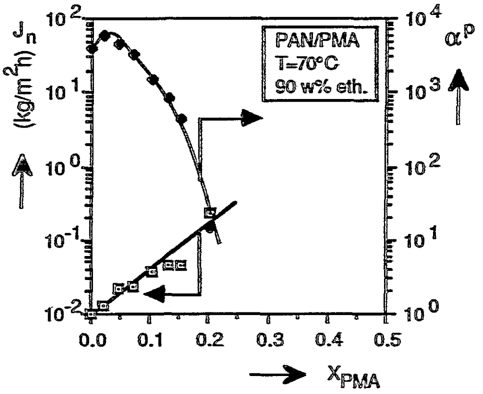


Figure 5.9: Normalized pervaporation flux J_n and selectivity α^P for a 90 w% ethanol/water mixture for PAN/PMA blend membranes, as a function of the composition X of the blend (weight fraction PMA).

Comparison between the PAN/PMA blend and the copolymer P(AN-MA)

In the next part the pervaporation properties of the PAN/PMA blend and the copolymer P(AN-MA) are compared. The composition of the copolymer was determined by NMR analysis: the weight fraction of maleic anhydride groups was about 0.10±0.02. The membrane prepared from the copolymer was also tested at 90 w% ethanol at 70°C. The results are presented in table 5.3. In this table also some interpolated results are given for two hypothetical PAN/PMA blends; one result for a blend membrane with the same flux as the copolymer, and one result for a blend membrane with the same selectivity as the copolymer.

Table 5.3: Comparison between the (interpolated) pervaporation properties of two PAN/PMA blend membranes and a copolymer P(AN-MA) membrane. Feed: 90 w% ethanol in water, 70°C.

	X (w.fr. PMA)	d (μm)	J_n (kg/m^{2}h)	α_p
copolymer	0.10	17	*0.014*	*2000*
blend	0.024	24	*0.014*	6000
	0.117	25	0.047	*2000*

From this table it can be concluded that at the same fluxes for the two membranes (blend and copolymer), the blend membrane has a three-fold higher selectivity. At the same selectivity the flux of the blend membrane is higher, again by a factor of about 3. Thus, in this case the pervaporation properties of the blend membrane are better than the properties of the copolymer membrane. The difference in pervaporation properties must be explained by differences in morphology of the polymer membranes. Whereas in the copolymer the hydrophilic PMA segments probably are arranged randomly, small microdomains of PMA can be present in the PAN matrix, which may lead to a different flux and selectivity characteristic. The only disadvantage of the blend membrane might be the long term stability, due to the possibility of washing out of the PMA. This long term stability can be improved by crosslinking the PMA.

Influence of the feed concentration

In the pervaporation experiments described so far two standard feed concentrations were used: 50 w% ethanol in water (at 25°C) and 90 w% ethanol in water (at 70°C). But the membrane properties often are strongly influenced by the feed concentration. For two blends (PAN/PVP= 85/15 and PAN/PMA=90/10) the flux and pervaporation selectivity were therefore determined as a function of the feed concentration, at 25°C. The results for these blend membranes are given in figure 5.10.

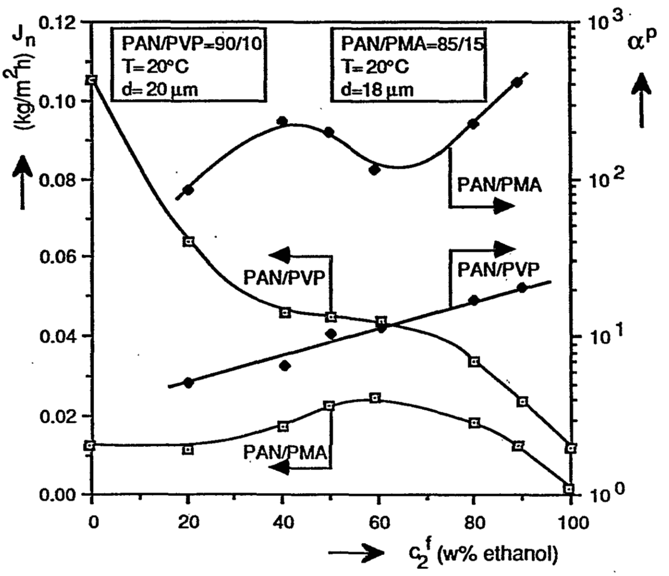


Figure 5.10: Normalized pervaporation flux J_n and selectivity α^P for membranes of the blends PAN/PVP and PAN/PMA, as a function of the feed concentration.

This figure shows that the fluxes of the PAN/PVP membranes are higher than those for membranes of PAN/PMA, despite the fact that the membrane contained a smaller fraction of hydrophilic polymer. This higher fluxes for the PAN/PVP blend membranes can be the result of the more bulky character of the side groups in PVP (leading to higher diffusion rates), but also to a difference in the interactions of the feed mixture with PVP or PMA, respectively. The flux of the PAN/PVP blend increases strongly with decreasing ethanol concentration in the feed, whereas the flux of the PAN/PMA blend is less sensitive to the feed concentration: the flux for pure water is about equal to the flux of a mixture containing 10 w% water.

The selectivities of the PAN/PMA blend membranes are higher, roughly by a factor of 10. The selectivity for both blends increases with increasing ethanol concentration in the feed, which is often found for water-selective membranes.

In figure 5.11 all pervaporation results for all blend membranes are replotted together. From the figure it can be seen that by using blends a great variety of fluxes and selectivities can be obtained: selectivities between $2<\alpha^P<6000$, and (normalized) fluxes between $0.01<J_n<2$ kg/m^{2}h. The figure shows that all the membranes show better performance at 70°C than at 25°C.

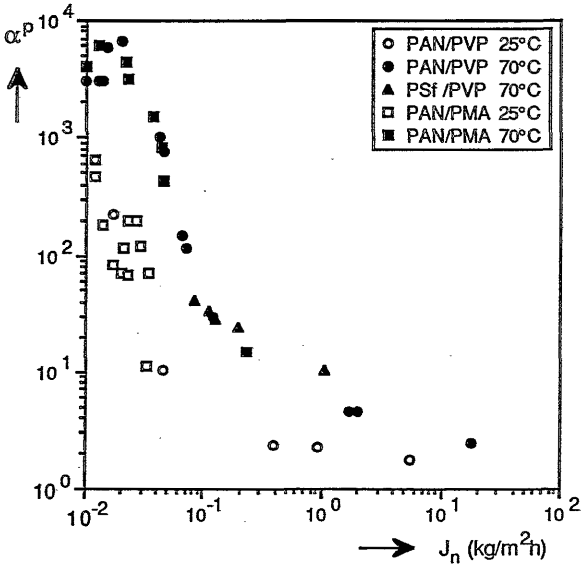


Figure 5.11: Summary of all pervaporation results with blend membranes.

Furthermore, it seems that (for constant feed conditions) the same combination of flux and selectivity can be obtained with every blend; only the composition of the blend seems to be important for a certain combination of flux and selectivity.

5.4.3 Sorption versus pervaporation

For the PAN/PVP blends the equilibrium sorption results can be compared to the pervaporation results, for 50 w% ethanol in water at 25°C.

By comparing figures 5.1 and 5.4 it can be seen that generally the total sorption Q and the permeation rate J follow the same trend: with increasing PVP content of the blend the total sorption and the permeation rate increase strongly. This is in agreement with the solution-diffusion model, because according to this model a higher concentration of the components in the membrane at the feed side (which can be related to the total sorption results) results in an increased permeation rate (see chapter 2 of this thesis).

Since at low PVP content in the blend ($X<0.10$) the total sorption is constant (see figure 5.1), the increase in the flux with increasing PVP content in that range must be explained by diffusional effects. This can be due to the fact that the monomeric unit of PAN is rather small, whereas the monomeric unit of PVP is bulky, because of the pyrrolidone group. So, at these low PVP contents PVP creates space for permeating molecules, leading to a (relatively modest) increase in flux. Because the increase of the component flux of ethanol is stronger than that of water, the selectivity decreases. At higher PVP contents in the blend the total sorption increases, and the selectivity drops strongly due to the plasticizing effect.

If it is assumed that the preferential sorption during pervaporation at the feed side of the membrane can be considered as equilibrium sorption, the preferential sorption results in figure 5.2 can be compared with the preferential permeation results in figure 5.4. In figure 5.12 both the pervaporation and the equilibrium sorption selectivity are plotted as a function of the blend composition. Also the ratio between the pervaporation selectivity and the equilibrium sorption selectivity is plotted; this ratio can be considered as a 'diffusion selectivity' α^d. This parameter can give some qualitative information about the diffusion phenomena taking place during the pervaporation process (see chapter 2 of this thesis).

$$\alpha^d = \alpha^p / \alpha^s \qquad (5)$$

From the figure it can be seen that at low PVP content of the membrane the effect of selective diffusion can not be neglected: selective diffusion of water (compared to ethanol) enhances the pervaporation selectivity. In pure PAN the pervaporation selectivity is mainly determined by the diffusion selectivity, rather than by the sorption selectivity. At increasing PVP content of the blend the influence of selective diffusion decreases. At even higher PVP content the diffusion selectivity is smaller than 1, which can be interpreted as a selective diffusion of ethanol. For X>0.3 all selectivities approach $\alpha=1$, which means that sorption, diffusion and permeation are non-selective, due to the excessive swelling of the membrane. It should be recognized that quantitative results calculated from equation (5) can only be used, if it is assumed that sorption of the components into the membrane during pervaporation can be considered as a thermodynamic equilibrium.

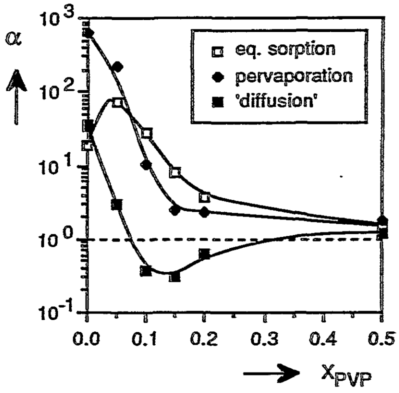


Figure 5.12: Equilibrium sorption selectivity, pervaporation selectivity and 'diffusion' selectivity for a 50 w% ethanol/water mixture for PAN/PVP blends, as a function of the composition X of the blend (weight fraction PVP).

5.4.4 Stability of the blends

Although a high molecular weight PVP was used, it is possible that at high concentrations of PVP in the blend, PVP will be washed out because it is soluble in both water and ethanol. The loss of PVP might influence the long term properties of these membranes during pervaporation. This phenomenon was investigated for the blends PAN/PVP and PSf/PVP.

For the PAN/PVP blends the PVP loss was determined during the equilibrium sorption experiments at 25°C (in 50 w% ethanol), as a function of the blend composition. The dry weight of the membranes was measured before and after the swelling in the mixture. Between these two measurements the membranes were immersed in the mixtures during eight months. The relative weight decrease of the membranes of different compositions is given in table 5.4. If it is assumed that the weight loss can only be due to the loss of the water-soluble PVP, the weight loss of PVP can be calculated. The table shows that the loss of PVP can be considerable, especially for the highest PVP content. These results can not be interpreted quantitatively, because the weight loss of PVP is dependent on the mixing conditions during the immersion period, which were not the same for all experiments.

Table 5.4: Weight loss of PAN/PVP blends, as a function of the composition of the blend, due to dissolution of PVP after immersion of the blend membranes during 8 months in a mixture of 50 w% ethanol in water at 25°C.

composition of the blend PAN/PVP (g/g)	relative weight decrease of the membrane (w%)	relative weight loss of PVP (w%)
100 / 0	0.3	-
95 / 5	1.1	22.6
90 / 10	1.7	16.7
85 / 15	0.8	5.4
80 / 20	0.6	3.1
50 / 50	19.5	39.0

The weight loss during pervaporation has also been determined, both for the PAN/PVP and PSf/PVP blend membranes containing 50 w% PVP. For a feed of 90 w% ethanol in water at 70°C the weight loss was determined after 1 hour and after 5 hours of pervaporation. The membranes were weighed before and after the experiment, and the results were corrected for the effective membrane area in contact with the feed solution. In table 5.5 the relative weight losses of PVP (compared to the original amount of PVP present in the membrane) for the membranes are given.

Table 5.5: Weight loss of membranes of PAN/PVP and PSf/PVP blends, due to dissolution of PVP during pervaporation. Feed: 90 w% ethanol in water, 70°C.

blend membrane (X=0.50)	t_{perv} (hr)	relative weight loss of PVP (w%)
PAN/PVP	1	20.5
PAN/PVP	5	22.1
PSf/PVP	1	40.1
PSf/PVP	5	65.4

From these results it is concluded that for both blends the loss of PVP is time dependent: after 5 hours of pervaporation more PVP is removed compared to 1 hour, especially for the PSf/PVP blend. Finally it is shown that the weight loss of PVP is smaller for the blend PAN/PVP, which is an indication for a better mixing of PAN and PVP at a molecular level.

From all results it is clear that these blend membranes can not be used at high PVP contents (X>0.20), because PVP is washed out of the membrane, and dissolves in the feed (as was observed by gas chromatography). The loss of PVP might be prevented by crosslinking of the PVP in the membrane phase. These membranes with high PVP contents, however, are not very interesting with respect to the pervaporation properties.

5.5 Conclusions

Transparent homogeneous blend membranes can be prepared from a highly water-selective, film forming polymer (low flux) and a hydrophilic (water soluble) polymer.

The equilibrium sorption experiments at 25°C using PAN/PVP blends showed that for increasing PVP content the total swelling increased strongly. For all blend compositions water was absorbed preferentially. At low PVP content (between 0 w% and about 5 w%) the equilibrium sorption selectivity is higher than that of pure PAN.

For all blends investigated (PAN/PVP, PSf/PVP and PAN/PMA) water permeated preferentially from a feed mixture of ethanol and water, both at 25°C and 70°C. Fluxes of highly selective membranes could be increased by increasing the content of hydrophilic polymer in the blend, which was explained by a combination of an increased sorption of the permeating molecules in the membrane and increased diffusion rates. The selectivity decreased for increasing content of the hydrophilic polymer, except for the blends PAN/PVP and PAN/PMA at 70°C, for which at low fractions of the hydrophilic polymer a maximum of the selectivity was found. So, for these two blends an optimal blend composition did exist: both flux and selectivity were increased by adding a small amount of hydrophilic polymer. Still, fluxes for these blend membranes remained at a low level.

By comparing the equilibrium sorption results with the permeation results at 25°C for the blends PAN/PVP the influence of selective diffusion of the components through the membranes was investigated. At low PVP content selective diffusion plays a role in the overall pervaporation performance. This influence decreased with increasing PVP content in the blends.

When the pervaporation properties of all blend membranes are compared with respect to flux and selectivity it was shown that indeed the flux or the selectivity can be adjusted to a desired level, simply by changing the homopolymers or the composition of the blends. Unfortunately no real improvement of the overall pervaporation properties were found: generally an increased flux resulted in a decrease of the selectivity and vice versa.

5.6 List of symbols

c_i = weight fraction of component i in the liquid (feed, permeate, membrane) (g/g)
d = membrane thickness (μm)
ΔG_m = free enthalpy of mixing (cal/g)
ΔH_m = enthalpy of mixing (cal/g)
ΔH^*_m = enthalpy of mixing, due to specific interactions (cal/g)
J = total pervaporation flux (kg/m^2h)
J_i = pervaporation flux of component i (kg/m^2h)
J_n = total pervaporation flux, normalized to 10 μm membrane thickness (kg/m^2h)
M_u = molecular weight of a component, or
the molecular weight of the monomeric unit of a polymer (Dalton)
Q = total sorption in the polymer: grams of absorbed liquid/gram dry polymer (g/g)
Q_i = component sorption of i in the polymer: gram absorbed i/gram dry polymer (g/g)
ΔS_m = entropy of mixing (cal/g.K)
V = volume of the blend (cm^3)
V_i = molar volume of component i (cm^3/mole)
X = weight fraction of hydrophilic polymer related to the total amount of
polymer in the casting solution (g/g)

α = selectivity (equilibrium sorption, pervaporation, diffusion) (-)
δ_i = solubility parameter of component i ($(cal/cm^3)^{1/2}$)
ϕ_i = volume fraction of polymer i in the blend (cm^3/cm^3)
ρ = density (g/cm^3)

subscripts
e = ethanol
m = mixing
w = water

superscripts
d = diffusion
f = feed
m = membrane
p = permeate, pervaporation
s = sorption

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Chapter 6

The effect of concentration polarization on pervaporation results.

J.W.F. Spitzen, M.J. van der Waal, M.H.V. Mulder, C.A. Smolders

Summary

Equations are derived for calculating concentration polarization at the feed side of a semi-permeable membrane in pervaporation processes. For concentration independent liquid densities and diffusion coefficients the equation derived here is similar to the equation commonly used for microfiltration, ultrafiltration and reverse osmosis. From this simplified equation the effects of parameters such as mass transfer coefficient, flux, selectivity and feed concentration on the actual flux and selectivity are calculated. The calculations showed that using recently developed pervaporation membranes with high flux and selectivity values, concentration polarization may play an important role and leads to decreased flux and selectivity values. Furthermore it is shown that at very low feed concentrations of the preferentially permeating component concentration polarization can play a role even at low flux values.

6.1 Introduction

Concentration polarization is a phenomenon that takes place when mass transfer of the components in the feed towards a semi-permeable membrane wall is among others rate limiting for the transport rate through the membrane. This phenomenon is inherent to all membrane separation processes and is well known from already commercialized membrane processes such as microfiltration (MF), ultrafiltration (UF) and reverse osmosis (RO). For these processes concentration polarization can be a serious problem, leading to a decrease in flux and separation characteristics.

For recently developed membrane processes such as gas separation and pervaporation it is generally assumed that concentration polarization does not play a role, because of the relatively low transport rates for these processes; only very few experimental results have been published in literature for these two membrane processes [6.1-6.5], from which it is evident that concentration polarization can not be neglected in all cases. Furthermore, mass transfer for low molecular weight components in liquids and gases is much faster than for solutions of polymers or colloids, or for solid particles in suspensions (such as in boundary layers for MF and UF), because of higher diffusion coefficients: $D \approx 10^{-9}$ m^2/s for low molecular weight components in liquids and $D \approx 10^{-11}$ m^2/s for suspended solids or colloidals. Since fluxes of recently developed membranes for pervaporation are much higher, in combination with high separation factors [6.6], it is necessary to realize that concentration polarization can influence the experimental results. In small scale laboratory set-ups concentration polarization can be influenced easily using a well mixed or stirred cell. When upscaling takes place to commercial plants (with more complicated membrane configurations and with less well-defined mass transfer conditions, such as dead volumes, fouling), concentration polarization can be avoided by applying high cross-flow velocities or mixing rates, resulting in additional energy consumption of the process.

In this chapter a general equation describing concentration polarization for pervaporation processes will be derived. This equation is solved for different levels of complexity. These different solutions are discussed and compared with the equation used for MF, UF and RO. In some numerical examples the influence of parameters such as mass transfer coefficient, bulk feed composition and membrane properties (flux and intrinsic selectivity) on the actual flux and selectivity in pervaporation will be presented.

6.2 Theory

General

In literature many relations have been developed describing concentration polarization during transport of solutions through semi-permeable membranes. These relations have mainly been developed and used for processes like MF, UF and RO, in which components (salts, colloids, macromolecules or cellular materials) are dissolved at low concentrations in the feed. In most cases the solute concentration is relatively low, and the solute is rejected by the membrane to some extent, whereas the solvents can permeate preferentially. The general equation [6.7] used is:

$$J^v.\delta/D_s = \ln\left((c^w - c^p)/(c^b - c^p)\right) \tag{1}$$

In this equation J^v represents the volume flux through the membrane, δ is the thickness (m) of the laminar boundary layer, D_s is the diffusion coefficient (m^2/s) of the solute in the solution, and c^w, c^p and c^b represent the concentrations (g/l, mole/l) of the rejected solute at the membrane wall, in the permeate and in the bulk feed solution, respectively. This equation is derived using the following assumptions:

1) The diffusion coefficient of the solute is constant (independent of concentration).
2) The density of the solution is constant, and equal to the density of the pure solvent.
3) The mass transfer coefficient is independent of the flux and concentration.

In equation (1) the wall concentration c^w determines the effect of concentration polarization, and it causes a decrease of fluxes in MF, whereas in UF and RO both the flux and the retention decrease. In MF and UF also a gel-type precipitate can be formed, which results in an additional hydrodynamic resistance [6.8].

Equation (1) can also be used for pervaporation, however, for convenient use it needs some elaboration. First, in pervaporation the units, in which fluxes and concentrations are expressed, are different from to those in MF, UF and RO. In pervaporation the concentrations of feed and permeate are generally expressed as weight fractions, because this is more convenient for liquid mixtures; pervaporation fluxes are generally expressed by mass fluxes, also for convenience. Furthermore, during pervaporation a phase transition occurs: the feed is a liquid, the permeate is a vapour. This may lead to confusion about the fact whether the permeate should be considered as a liquid or as a vapour. Finally, in most cases both diffusion coefficients and liquid densities can be dependent on the concentration of the liquid mixture.

A *general* equation for calculating concentration polarization during pervaporation and other membrane processes will be derived here for a binary feed mixture, in which the fluxes and the concentrations are expressed as mass flows and weight fractions, respectively. From this general equation some special cases will be discussed.

Concentration polarization in pervaporation

In pervaporation of a binary liquid mixture (components 1 and 2) both components are permeating through a semi-permeable membrane. Generally the permeation rates of the two components are different. This results in an increase in concentration of the less permeable component (component 2) at the membrane wall at the feed side, and a concentration gradient will develop. This is represented schematically in figure 6.1. The flows J are represented as volume flows (m^3/m^2h), the concentrations c are given in volume fractions ϕ_i (m^3/m^3). Because the concentration of the less permeable component at the membrane wall is higher than in the bulk feed, diffusion of component 2 back into the feed will take place. Simultaneously there is a diffusional flow of component 1 from the bulk feed towards the membrane wall.

Consider the volume element at the feed side of the membrane in figure 6.1, between x=0 and $x=x_1$, with a constant area parallel to the membrane. In this situation three different *volume* flows can be distinguished (mass transfer due to density or temperature gradients is neglected):

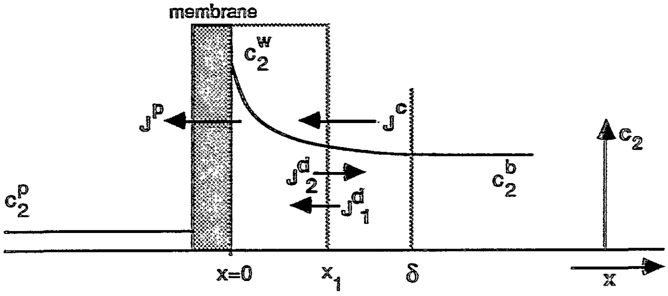

Figure 6.1: Concentration profile of the less permeable component 2 of a liquid mixture, in contact with a semi-permeable membrane.

a) *Convective* flow of the components towards the membrane, denoted by J^c.

This flow is a result of the removal of components from the feed by permeation through the membrane.

b) *Diffusional* flow of the components in the boundary layer, denoted by J^d.

This flow is due to the concentration gradients of the components in the boundary layer.

c) *Permeation* of the components through the membrane, denoted by J^p.

This flow is due to the concentration gradient of the components inside the membrane itself.

In the stationary state both the volume and the mass of this volume element must be constant. The *volume* balances over this volume element are:

Total: $J^c - J^d - J^p = 0$ (2)

Component i: $J^c_i - J^d_i - J^p_i = 0$ (i=1,2) (3)

J^c_i, J^d_i, and J^p_i are the component flows due to convection, diffusion and permeation, respectively. The component flows due to diffusion are described by Fick's law:

$$J^d_1 = - D^v . d(\phi_1(x))/dx \qquad (4a)$$

$$J^d_2 = - D^v . d(\phi_2(x))/dx \qquad (4b)$$

Whereas in this case the diffusion law is applied to volume units, in appendix A a survey is given on the different representations of this law for other units (such as mass flows and molar flows).

In equations (4a) and (4b) $\phi_i(x)$ represents the volume fraction of component i in the liquid mixture. Since at every distance from the membrane the total concentration $\phi_1(x)+\phi_2(x)=1$, combination of equations (4a) and (4b) leads to:

$$J^d_1 + J^d_2 = J^d = 0 \qquad (5)$$

This means that the diffusional flow of component 2 (J^d_2) back into the bulk feed is counterbalanced by a diffusional flow of component 1 (J^d_1) towards the membrane. Combination of equations (2) and (5) leads to:

$$J^c - J^p = 0 \quad \text{or} \quad J^c = J^p \qquad (6)$$

The different flows of component 2 can be calculated as follows:

convection: $J^c_2 = J^c . \phi_2(x)$ (7)

permeation: $J^p_2 = J^p . \phi_2^p$ (8)

diffusion: $J^d_2 = - D^v . d(\phi_2(x))/dx$ (4b)

In spite of the fact that the permeate in pervaporation always is a vapour, the permeate has to be considered as a *liquid* in equation (8), because volume flows in the volume element in the liquid phase are considered.

Combination of equations (3),(4b),(6-8) leads to the most general form of the component volume balance describing concentration polarization, taking the permeate flow J^p as the overall volume flux J^v:

$$J^v.\left(\phi_2(x) - \phi_2^p\right) = - D^v . d\left(\phi_2(x)\right)/dx \qquad (9)$$

The boundary conditions for this equation are (using the film model):

$x = 0$: $\phi_2 = \phi_2^w$ (10a)

$x = \delta$: $\phi_2 = \phi_2^b$ (10b)

δ is the thickness of the laminar boundary layer.

In equation (9) the flux J^V does not depend on x and on c_i (total flux is constant in the boundary layer and is only dependent on the wall concentration $\phi_i^w = \phi_i(x=0)$ of the components). On the other hand, the diffusion coefficient D^V generally is a function of the concentration ϕ_i in the boundary layer. The most simple solution of the differential equation (9) is obtained if a constant diffusion coefficient is assumed. In case the diffusion coefficient in the liquid is dependent on the concentration, as a first approximation a linear relationship can be used, because the concentration gradient in the boundary layer is relatively small. The solution of equation (9) for this case is given in appendix B.

For a constant diffusion coefficient equation (9) can easily be solved by integration. By rearrangement the following integral solution is found:

$$\int_0^{\delta} J^V . dx = - D^V . \int_{\phi_2^w}^{\phi_2^b} (\phi_2(x) - \phi_2^p)^{-1} . d\phi_2(x) \qquad (11)$$

$$J^V . \delta / D^V = \ln \{(\phi_2^w - \phi_2^p)/(\phi_2^b - \phi_2^p)\} \qquad (12)$$

Equation (12) is similar to equation (1), but to derive equation (12) we did not have to assume a constant density.

According to the film theory, the thickness of the boundary layer δ can be related to the mass transfer coefficient k:

$$D^V/\delta = k \qquad (13)$$

Substitution of k into equation (12) gives the final equation for the case of a constant diffusion coefficient, from which the concentration of the components at the membrane wall can be calculated:

$$J^V/k = \ln \{(\phi_2^w - \phi_2^p)/(\phi_2^b - \phi_2^p)\} \qquad (14)$$

To use this equation for pervaporation purposes, for convenience the volume fractions (ϕ_i) will be converted into weight fractions (w_i), and the volume flux J^V into a mass flux J^m. If the density of the liquid mixture is represented by ρ, and ρ_i is the density of pure component i, it can be derived that $\rho_i\phi_i=\rho w_i$, when it is assumed that the molar volume of the pure component i is equivalent to the partial molar volume of this component in the mixture. The volume flux is converted into a mass flux using the density ρ^p of the permeate as a liquid. Hence, the most general equation for concentration polarization with a concentration independent diffusion coefficient is:

$$J^m/(k.\rho^p) = \ln\left\{(\rho^w w_2^w - \rho^p w_2^p)/(\rho^b w_2^b - \rho^p w_2^p)\right\} \qquad (15)$$

In this equation ρ^p, ρ^b and ρ^w represent the densities of the permeate, bulk feed and feed at the membrane wall, respectively.

In the case of *constant liquid density* ρ this equation can be simplified to:

$$J^m/(k.\rho) = \ln\left\{(w_2^w - w_2^p)/(w_2^b - w_2^p)\right\} \qquad (16)$$

Although this simplified equation can be used in some cases, generally the density of a liquid mixture is a function of the concentration of the mixture. In the case of *concentration dependent liquid density*, equation (15) generally has to be solved by trial and error.

To illustrate the effect of a concentration dependent density two situations will be compared, assuming the same concentrations in the bulk feed, at the membrane wall and in the permeate: $w_2^w=0.8$, $w_2^b=0.6$, $w_2^p=0.5$.

In the first situation a *constant* density will be assumed; in the other situation the density is assumed to be *linearly dependent* on the concentration (weight fraction) of the liquid. It is assumed that the density of the preferentially permeating component 1 is higher than the density of the less permeable component 2: $\rho_1=1000$ kg/m^3 and $\rho_2=800$ kg/m^3. In that case the densities of the bulk feed, at the membrane wall and of the permeate are: $\rho^w=840$ kg/m^3, $\rho^b=880$ kg/m^3 and $\rho^p=900$ kg/m^3. In the case of a constant liquid density, the density is taken as $\rho=840$ kg/m^3, being the density of the liquid at the membrane wall for the case of a concentration dependent density. A mass transfer coefficient of $k=10^{-6}$ m/s is taken. Using equation (16) for a *constant density*, a mass flux of $J^m=3.322$ kg/m^{2}h is calculated. Using the equation (15) for a *concentration dependent density*, the mass flux is $J^m=3.389$ kg/m^{2}h (taking ρ linearly dependent). Hence, the same concentration polarization is already reached at lower fluxes in the case of a constant density; the effect, however, is very small.

If the density of component 1 is lower than the density of component 2 ($\rho_1=800$ kg/m^3 and $\rho_2=1000$ kg/m^3), the reverse situation is found: the same concentration polarization is reached at lower fluxes in the case of a concentration dependent density.

Influence of different parameters on concentration polarization

Not only the liquid density influences the effect of concentration polarization. From equation (15) it is seen that concentration polarization is also influenced by:

- the mass transfer coefficient k
- the flux through the membrane J
- the *bulk feed concentration* c_i^b
- the intrinsic membrane selectivity α (which determines the relation between c_i^w and c_i^p):

$$\alpha = (c_1^p/c_2^p)/(c_1^w/c_2^w) \qquad (17)$$

In the following paragraph the effects of the parameters mentioned above will be shown by some numerical examples. To demonstrate the effects qualitatively, the case of a *constant* diffusion coefficient and *constant* liquid density was studied.

*It should be mentioned that also the feed temperature can influence concentration polariza*tion. When the feed temperature is increased, generally pervaporation fluxes increase and liquid densities decrease. For a given module design and flow velocity in the module, the feed temperature affects the mass transfer coefficient k through the diffusion coefficient and the viscosity of the feed. It can be deduced that an increase of the feed temperature generally leads to an increase of k. Considering these antagonistic effect of temperature on flux, density and mass transfer coefficient, it can not be predicted on forehand, whether an increase of the feed temperature leads to a higher or a lower concentration polarization (see equation (15) or (16)).

6.3 Calculations

The main factor determining concentration polarization is the *mass transfer coefficient*, which is governed by the mixing conditions in the feed near the membrane surface. These mixing conditions are influenced by the flow conditions of the feed (stirring, flow velocity, turbulence promotion) and the module design. A typical value for the mass transfer coefficient in liquids is $k=10^{-5}$ m/s, but this value can be higher or lower (see appendix D). In our calculations mass transfer coefficients of $k=10^{-8}$, 10^{-7},10^{-6} and 10^{-5} m/s are chosen. Although the values of 10^{-7} and 10^{-8} are extremely low, these values were taken to investigate the effect of concentration polarization for the cases when hardly any mixing takes place. In the calculations the mass transfer coefficient was kept constant. It should be kept in mind that k can be dependent on the flux and the concentration (through the diffusion coefficient and the viscosity).

From equation (16) it follows that also the *flux* level determines concentration polarization: concentration polarization increases with increasing flux. In the calculations the influence of concentration polarization will be demonstrated as a function of the flux, for chosen values of other parameters that also determine concentration polarization. The fluxes ranged from low values of J=0.001 kg/m^{2}h to extremely high values J=1000 kg/m^{2}h. Although fluxes of J=1000 kg/m^{2}h are not realistic for pervaporation, the calculations were extended to these high values, to investigate the trends and limits of the model. It is recognized that nowadays pervaporation fluxes are of the order of magnitude of J=0.01-10 kg/m^{2}h.

Because the flux decrease due to concentration polarization is influenced by the flux itself, we will discriminate between the *ideal flux* and the *actual flux*. The ideal flux (represented by J) is defined as the flux for the case of no concentration polarization. The actual flux (represented by J*) can be measured experimentally and is influenced by concentration polarization.

From equation (16) it can be seen that also the bulk *feed concentration* has an influence on concentration polarization. In the examples bulk feed concentrations of c_i^b=0.01, 0.10, 0.20 and 0.50 (weight fractions) are chosen.

Although it follows not directly from equation (16), concentration polarization is also influenced by the intrinsic membrane *selectivity* α.

The selectivity is determined by the differences in permeation rates of the components through the membrane. The wall concentrations of both components will depend on the membrane selectivity, and therefore the actual flux and selectivity are influenced by the intrinsic membrane selectivity.

Because the selectivity due to concentration polarization is influenced by the membrane selectivity itself, we will discriminate between the *ideal selectivity* and the *actual selectivity*. The ideal selectivity is the intrinsic selectivity (represented by $\alpha=(c_i^p/c_j^p)/(c_i^w/c_j^w)$) and is by definition not influenced by concentration polarization. The actual selectivity (represented by α^*) is measured experimentally and is influenced by concentration polarization; this selectivity is based on the bulk feed concentration and the actual permeate concentration: $\alpha^*=(c_i^p/c_j^p)/(c_i^b/c_j^b)$. In the examples intrinsic membrane selectivities of α=9, 99, 999 and 9999 are chosen.

We recapitulate the assumptions used for the numerical calculations:

- The density ρ of the liquid mixture is independent of the concentration of the mixture, and equals to ρ=1000 kg/m^3.
- The intrinsic membrane selectivity α is independent of the concentration at the membrane wall.
- The mass transfer coefficient k is independent of the concentration of the mixture.
- The flux J is a linear function of the concentrations at the membrane wall:

$$J = c_1^{w} . J_1^{o} + c_2^{w} . J_2^{o} \qquad (18)$$

The pure component fluxes J_1^o and J_2^o are always chosen such that the total flux is equal to the ideal flux (no concentration polarization), and the ratio of these pure component fluxes is equal to the intrinsic membrane selectivity α (see appendix C). This means that the values of J_1^o and J_2^o have been changed during the calculations, as the total flux, the bulk feed concentration and the intrinsic membrane selectivity have been varied.

Using the assumptions mentioned above, concentration polarization always will result in lowered fluxes and selectivities. It should be noted that in practical situations these simple assumptions do not always hold, and other relations between flux or selectivity and feed concentration exist.

In many practical cases the selectivity increases with increasing concentration of the less permeable component. In those cases the decrease of the experimental selectivity, due to concentration polarization, will be smaller. It is even possible that due to a strong increase of the intrinsic selectivity with feed concentration the experimental selectivity increases too.

Although fluxes generally decrease with increasing concentration of the less permeable component, it is possible that in some concentration ranges the flux increases [6.9,6.10]. In that case concentration polarization leads to higher fluxes.

The calculations are performed using equation (16). The mass flux J^m will be represented by J, the concentrations (weight fractions) by c. Because some parameters (flux and permeate concentration) in this equation are generally dependent on the concentration at the membrane wall, equation (16) has to be solved by iteration. So, the wall concentration, as the most important parameter, has been determined by trial and error.

6.4 Results and discussion

Influence of the flux on c_1^w, c_1^p, J^* and α^*

In a few examples the effect of concentration polarization on several pervaporation parameters will be demonstrated. In the first examples the following parameters are chosen: c_1^b=0.50, α=99, and k=10^{-6} m/s.

Since the intrinsic membrane selectivity is taken constant, the permeate concentrations will change due to a change in the wall concentration. In figure 6.2 both the wall concentration c_1^w and the actual permeate concentration c_1^p of the preferentially permeating component are given as a function of the ideal flux.

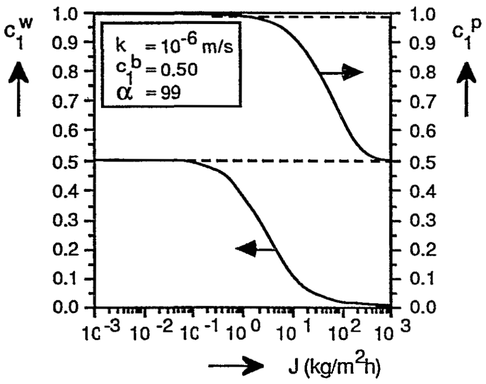

Figure 6.2: Concentration (weight fraction) of the preferentially permeating component at the membrane wall c_1^w and in the permeate c_1^p, as a function of the ideal flux J.

At low fluxes the wall concentration is equal to the bulk feed concentration ($c_1^w = c_1^b = 0.50$). When the flux increases, the wall concentration remains about constant, until at a certain flux (in this case about J=0.1 kg/m²h) the wall concentration of the preferentially permeating component decreases; due to this decrease also the permeate concentration of this component decreases. At higher fluxes the wall concentration drops to a very low value and the permeate concentration decreases to the bulk feed concentration (as can be deduced from equation (16): $J/\rho.k \rightarrow \infty$ for maximum concentration polarization). At these high fluxes the membrane shows virtually no selectivity at all (based on the bulk concentrations). So, at maximum concentration polarization the wall concentration c_1^w will not decrease to zero, but to a value that is determined by the intrinsic membrane selectivity (and the bulk feed concentration), so that the permeate composition equals that of the feed bulk. In this case the wall concentration decreases to $c_1^w = 0.01$.

Since the actual flux is dependent on the wall concentrations, the flux decrease due to concentration polarization is dependent on the ideal flux values (in fact, in equation (16) J^m represents the actual flux J^*). In most cases fluxes decrease with decreasing concentration of the preferentially permeating component; therefore fluxes will generally decrease when concentration polarization takes place. In figure 6.3a the actual flux is given as a function of the ideal flux. At low fluxes (no concentration polarization) the actual flux equals the ideal flux. In this flux range the total transport rate is only determined by the membrane properties. At higher fluxes mass transfer of the components towards the membrane becomes rate determining, and the actual flux will be lower than the ideal flux. When concentration polarization increases, the wall concentration of the preferentially permeating component c_2^w will decrease to low values, and the actual flux will approach the flux of the pure, less permeable component. For $J \rightarrow \infty$ it can be derived that $J^*/J \rightarrow \alpha / (\alpha + (\alpha-1)^2.c_1^b.c_2^b)$; in this case $J^*/J \rightarrow 0.0396$. Hence, the flux ratio will never decrease to zero at high ideal fluxes.

Since the permeate concentration changes with concentration polarization, also the actual (or apparent) selectivity α^* (based on the bulk concentration in the feed and the permeate concentration) will change. This can be seen from figure 6.3b: at low fluxes the actual selectivity α^* is about constant and equal to the intrinsic membrane selectivity α, but with increasing flux the actual selectivity decreases, to reach finally α^*=1 (bulk feed concentration and permeate concentration become equal).

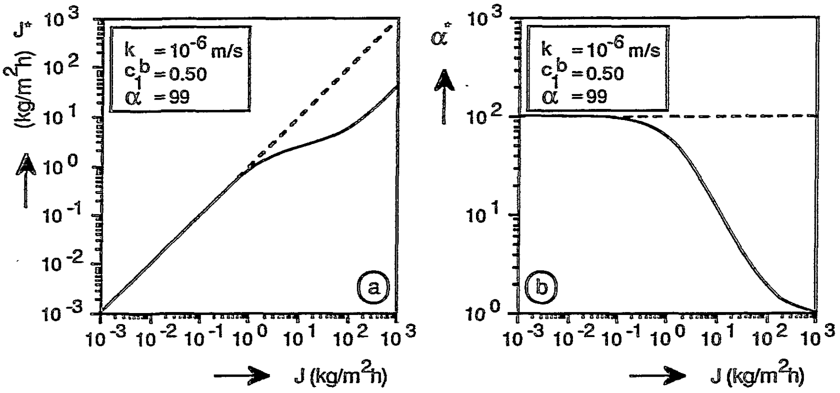

Figure 6.3: Actual flux J^* (a) and actual selectivity α^* (b), as a function of the ideal flux J.

We will now discuss the effect of membrane thickness. When the thickness of a membrane is reduced, e.g. in order to increase the flux of a very selective membrane, concentration polarization will increase. In that case the actual flux will be lower than expected on the basis of the reciprocal relation between flux and membrane thickness. But more important, the actual selectivity of a thin membrane will be lower than for thicker membranes. This is demonstrated in figure 6.4, where the actual flux and actual selectivity are presented as a function of the membrane thickness, for a membrane with an ideal flux of J=0.1 kg/m^{2}h at a thickness of 10 µm. The fluxes a other thicknesses are calculated using the reciprocal relation between the ideal flux and membrane thickness (J~1/d). From these figures it follows that for thin membranes lower fluxes and selectivities are found, as expected.

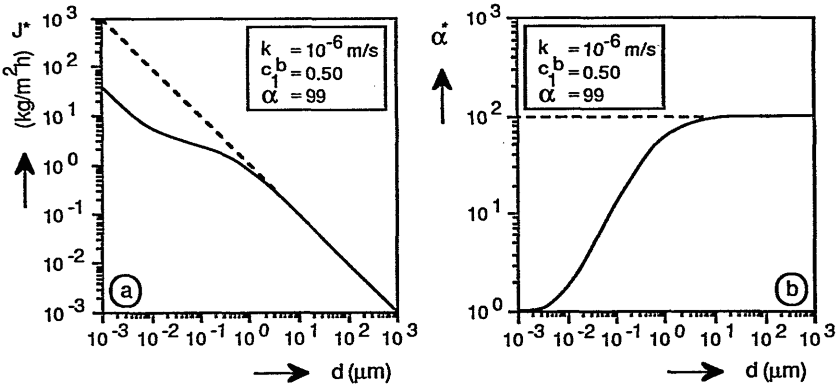

Figure 6.4: Actual flux J^* (a) and actual selectivity α^* (b), as a function of membrane thickness d. Ideal flux J proportional to reciprocal thickness 1/d (J=0.1 kg/m²h at d=10 μm).

Influence of the mass transfer coefficient k

Until now the influence of concentration polarization was demonstrated for only one value of the mass transfer coefficient k. The results were presented as a function of the (ideal) flux (or reciprocal thickness) and because this flux also determines the effect of concentration polarization, the effect of low and high concentration polarization on the process could be demonstrated.

Now the influence of concentration polarization will be given for different mass transfer coefficients, for different intrinsic membrane selectivities and for different feed concentrations. For practical reasons only the results for the actual flux and actual (apparent) selectivity as a function of the (ideal) flux are presented.

In figure 6.5 the actual selectivity and actual flux are given as a function of the ideal flux, for four different mass transfer coefficients, ranging from $k=10^{-8}$ to $k=10^{-5}$ m/s. The bulk feed concentration is $c_1^b=0.50$, the intrinsic membrane selectivity is $\alpha=99$.

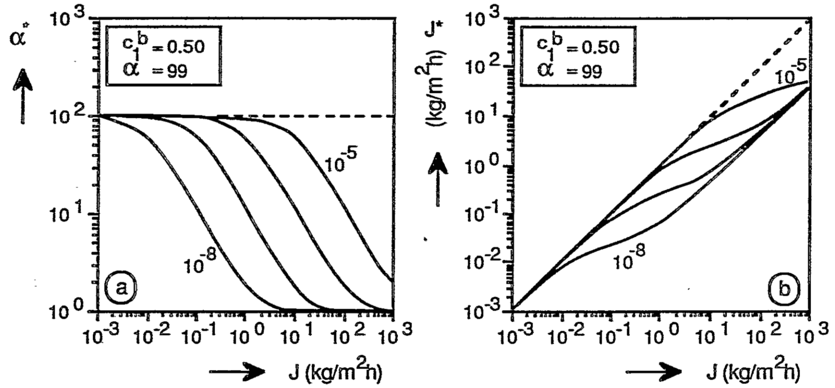

Figure 6.5: Actual selectivity α^* (a) and actual flux J^* (b), as a function of the ideal flux J, for different mass transfer coefficients: $k=10^{-8}$, 10^{-7}, 10^{-6} and 10^{-5} m/s.

From figure 6.5a it can be seen that the actual selectivity decreases with increasing flux. This decrease already starts at low fluxes for low mass transfer coefficients. Because pervaporation fluxes of more recently developed membranes are in the range of J=0.1 to 10 kg/m^{2}h, it is clear that concentration polarization plays a role, when the mass transfer coefficient is lower than $k=10^{-6}$ m/s. However, for very high fluxes the actual selectivity vanishes ($\alpha^*=1$), for all mass transfer coefficients.

Figure 6.5b shows that, at nowadays realizable pervaporation fluxes, flux decrease will take place for $k<10^{-6}$ m/s. The flux decrease is 3 to 23% for J=0.1 kg/m^{2}h and 23 to 77% for J=1.0 kg/m^{2}h, for $k=10^{-6}$ to 10^{-7} m/s respectively. This relative flux decrease is strongly dependent on the intrinsic membrane selectivity, as will be shown later. For high fluxes the ratio of the actual and ideal flux reaches a constant level (determined by the intrinsic selectivity), which is the same for all mass transfer coefficients. This ratio is for the parameters here assumed: $J^*/J=0.0396$.

It should be recognized that in general mass transfer coefficients of the order of magnitude of $k=10^{-5}$ m/s are more realistic. From figure 6.5 it is concluded that in those cases, with nowadays pervaporation fluxes lower than 10 kg/m^{2}h, the effect of concentration polarization generally can be neglected. However, the following calculations are performed using $k=10^{-6}$ m/s, to show the effect of concentration polarization if the mixing conditions near the membrane are not optimal.

Influence of intrinsic membrane selectivity α

In figure 6.6 the actual selectivity and actual flux are given as a function of the ideal flux, for four membranes with different intrinsic membrane selectivities, ranging from α=9 to α=9999. The bulk feed concentration is again $c_1^b=0.50$, the mass transfer coefficient is $k=10^{-6}$ m/s.

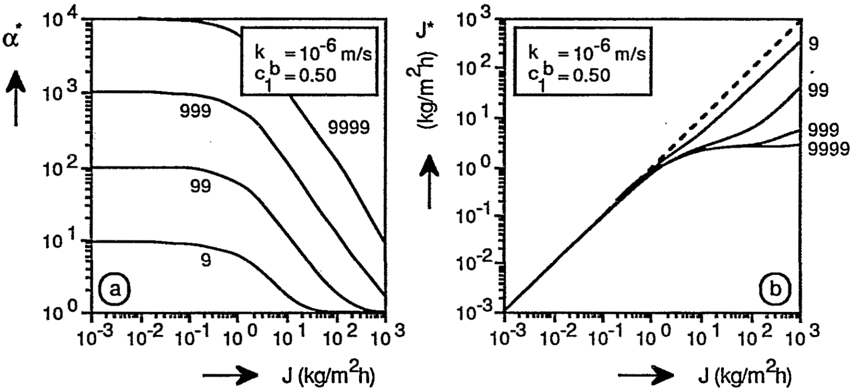

Figure 6.6: Actual selectivity α^* (a) and actual flux J^* (b), as a function of the ideal flux J, for different intrinsic membrane selectivities: α=9, 99, 999 and 9999.

Figure 6.6a shows that the actual selectivity decreases strongly with increasing flux. The decrease in selectivity starts at roughly the same flux for all 4 membranes, at about J=0.1 kg/m^{2}h (for this mass transfer coefficient). The absolute decrease in selectivity is more severe for more selective membranes. The selectivity decreases by a factor of 2.5 when the flux increases from J=0.2 to 2 kg/m^{2}h. In practical cases (fluxes lower than J=10 kg/m^{2}h) the selectivity for a very selective membrane (and for this mass transfer coefficient) remains at a high level; at lower values of k the decrease in selectivity can be more dramatic (see figure 6.5a). For high enough fluxes the actual selectivity for all 4 membranes will decrease to $\alpha^*=1$.

From figure 6.6b again it can be seen that flux decrease due to concentration polarization can take place at fluxes higher than about J=1 kg/m^{2}h. This flux decrease is more severe for the more selective membranes, because when concentration polarization takes place, the flux will decrease to the flux value for the less permeable component. Because the membranes are compared at the same total (ideal) flux, the flux of the less permeable pure component is lower for more selective membranes. Hence, for more selective membranes not only the selectivity decrease can be important, but also the flux decrease can be considerable. From figure 6.6b it can be seen that the actual flux reaches a constant level for high ideal fluxes and increasing selectivities. This constant level of J^* can be calculated from equation (16): if the intrinsic membrane selectivity increases, c_2^w will increase to 1 and c_2^p will decrease to 0. This means that $J^*/\rho.k$ approaches $\ln(1/c_2^b)$. In our case, with c_2^b=0.5, ρ=1000 kg/m^3, and k=10^{-6} m/s the actual flux will have its plateau level at J^*=2.495 kg/m^{2}h.

Influence of the feed bulk concentration

In figure 6.7 the actual selectivity and actual flux are given as a function of the ideal flux, for four bulk feed concentrations, ranging from c_1^b=0.01 to c_1^b=0.50. The mass transfer coefficient is $k=10^{-6}$ m/s, the intrinsic membrane selectivity is α=99.

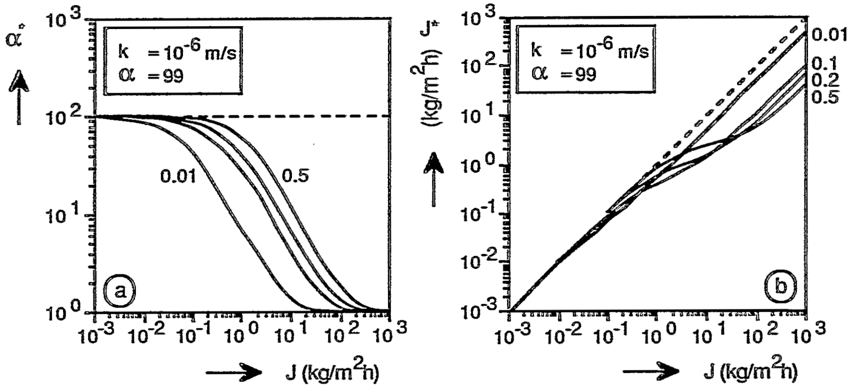

Figure 6.7: Actual selectivity α^* (a) and actual flux J^* (b), as a function of the ideal flux J, for different bulk feed concentrations: c_1^b=0.01, 0.1, 0.2 and 0.5.

Figure 6.7a shows that the actual selectivity already decreases at low flux levels for low concentrations of the preferentially permeating component. This can be an important problem for pervaporation of dilute organic compounds in water with elastomeric membranes: in those cases generally low fluxes are combined with extremely high selectivities [6.11].

From figure 6.7b it can be seen that also the flux decrease already starts at low flux values for low feed concentrations (of the preferentially permeating component), but the flux decrease (at high ideal fluxes) is smaller for these lower feed concentrations. This can be explained by the fact that at lower feed concentrations the absolute decrease in wall concentration c_1^w will be very small, so that the actual flux (linearly dependent on the wall concentration) is almost equal to the ideal flux. Again, it can be seen that at high ideal fluxes the ratio between the actual and ideal flux J^*/J approaches constant values, which are dependent on the feed concentration and the intrinsic membrane selectivity. This constant ratio is: $J^*/J = \alpha / (\alpha + (\alpha-1)^2 . c_1^b . c_2^b)$.

6.5 Conclusions

In the first part it was shown that the equation that usually is employed to calculate concentration polarization (for MF, UF and RO), generally can also be used for pervaporation. As the dimensions for flux and concentration used in pervaporation and MF, UF and RO are different, a more convenient form of the equation is derived. An adequate equation for pervaporation is still to be obtained, if the concentration dependence of liquid density and of diffusion coefficient are not known on forehand.

At concentration independent liquid density and constant diffusion coefficient a simple equation was derived, which can be used to describe concentration polarization in pervaporation processes. Using this simple expression (16) the consequences of concentration polarization phenomena on pervaporation performance have been obtained.

The calculations presented show clearly that, although usually the fluxes in pervaporation are much lower than for MF, UF and RO, in certain cases concentration polarization can be expected to have a strong influence on the actual results in pervaporation processes, and can not be neglected 'a priori'.

The calculations show further that concentration polarization generally leads to decreased fluxes and selectivities; these effects increase with:

a) decreasing mass transfer coefficient
b) increasing flux
c) increasing intrinsic membrane selectivity
d) decreasing concentration of the preferentially permeating component

6.6 List of symbols

c = *concentration* (kg/kg, m^3/m^3, mole/l, g/l)
d = membrane thickness (μm)
d_h = hydraulic diameter (m)
D^v = fixed volume diffusion coefficient (m^2/s)
J = ideal pervaporation flux (*without* concentration polarization) (kg/m^{2}h, m^3/m^{2}h, mole/m^{2}h)
J^* = actual pervaporation flux (*with* concentration polarization) (kg/m^{2}h, m^3/m^{2}h, mole/m^{2}h)
J_i = pervaporation flux of component i (kg/m^{2}h, m^3/m^{2}h, mole/m^{2}h)
k = mass transfer coefficient (m/s)
L = channel length in membrane module (m)
m = *mole fraction* (mole/mole)
Re = Reynolds number (-)
Sc = Schmidt number (-)
V = molar volume (mole/m^3)
w = weight fraction (kg/kg)
x = distance from membrane wall (m)

α	=	pervaporation selectivity	(-)
δ	=	thickness of laminar boundary layer	(m)
ϕ	=	volume fraction	(m^3/m^3)
ρ	=	density	(kg/m^3)
ν	=	kinematic viscosity	(m^2s)

<u>subscripts</u>

i, j = components in the liquid mixture
1 = preferentially permeating component
2 = less permeable component
s = solute

<u>superscripts</u>

b = bulk feed solution
c = convection
d = diffusion
m = mass
M = molar
p = permeate, permeation
v = volume
w = membrane wall (at the feed side)
o = pure component
* = with concentration polarization

6.7 References

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6.8 Appendices

Appendix A: Diffusion law of Fick.

The first diffusion law of Fick represents the relationship between the diffusional flow and the driving force, which is a concentration gradient. The proportionality factor is the diffusion coefficient.

$$J_i = -D_i . dc_i/dx \qquad (A1)$$

This relation can be used to describe transport of mass, volume and moles, due to the corresponding concentration gradient. Because the dimension of the diffusion coefficient always is m^2/s, the following equations can be derived, representing the *volume* diffusion rate, the *mass* diffusion rate or the *molar* diffusion rate.

Volume flux: $J^v_i = -D_i . d\phi_i/dx$ (m^3/m^2s) (A2)

(ϕ_i = volume fraction of component i: m^3/m^3)

Multiplication of this equation with ρ_i (density of component i) results in the mass flux J^m_i, assuming no excess volumes: (with $\rho_i \phi_i = \rho w_i$, and ρ= density of the mixture: kg/m^3).

Mass flux: $J^m_i = -D_i . d(\rho w_i)/dx$ (kg/m^2s) (A3)

(w_i= weight fraction of component i: kg/kg)

Multiplication of equation (A2) with v_i (molar volume of component i) results in the molar flux J^M_i: (with $v_i \phi_i = v m_i$, and v= molar volume of the mixture: $mole/m^3$).

Molar flux: $J^M_i = -D_i . d(v m_i)/dx$ $(mole/m^2s)$ (A4)

(m_i= mole fraction of component i: mole/mole)

Appendix B: Equation for concentration polarization, with diffusion coefficient linearly dependent on concentration.

In paragraph 6.2 a simple equation for calculating concentration polarization was developed for the case of a constant diffusion coefficient in the liquid feed. In general the diffusion coefficient will be a function of the concentration. Because the concentration gradient in the boundary layer is relatively small, a linear relation between D^v and the concentration can be used as a first approximation:

$$D^v(\phi_2) = D_1^v . \phi_1 + D_2^v . \phi_2 = D_1^v + \phi_2 . \Delta D^v \qquad \text{(B1)}$$
$$\text{with } \Delta D^v = D_2^v - D_1^v$$

D_1^v and D_2^v are the diffusion coefficients of the pure components; these may be the actual diffusion coefficients or the extrapolated values from the linearization.

Because the mass transfer coefficient is related to the bulk conditions, in this case k is represented by:

$$k = (D_1^v + \phi_2^b . \Delta D^v) / \delta \qquad \text{(B2)}$$

Substitution of equations (B1) and (B2) into equation (9), and integration using the boundary conditions (10) results in:

$$J^v/k = \left\{(D_1^v + \phi_2^p . \Delta D^v)/(D_1^v + \phi_2^b . \Delta D^v)\right\} . \ln\left\{(\phi_2^w - \phi_2^p)/(\phi_2^b - \phi_2^p)\right\} +$$
$$+ \left\{\Delta D^v/(D_1^v + \phi_2^b . \Delta D^v)\right\} . (\phi_2^w - \phi_2^b) \qquad \text{(B3)}$$

This equation can easily be simplified to the case of constant diffusion coefficient, by taking $\Delta D^v = 0$. Equation (B3) reduces then to equation (14).

Appendix C: Relation between α and the pure component fluxes J_1^o and J_2^o.

The intrinsic membrane selectivity α is determined by the actual concentrations of the feed and permeate near the membrane wall:

$$\alpha = (c_1^p/c_2^p)/(c_1^w/c_2^w) \qquad \text{(C1)}$$

Because the permeate concentrations c_i^p are determined by the component fluxes J_i this can be rewritten as:

$$\alpha = (J_1/J_2)/(c_1^w/c_2^w) \qquad \text{(C2)}$$

If the flux is linearly dependent on the concentration of the components at the membrane wall, the component fluxes can be written as $J_1=c_1^w.J_1^o$ and $J_2=c_2^w.J_2^o$; so:

$$\alpha = (c_1^w.J_1^o/c_2^w.J_2^o)/(c_1^w/c_2^w) = J_1^o/J_2^o \qquad \text{(C3)}$$

Appendix D: Calculation of mass transfer coefficients in pervaporation.

As an example mass transfer coefficients are calculated for pervaporation of an ethanol/water mixture. The weight fraction ethanol in the mixture is $c_2^b=0.5$, the temperature is 25°C. For the calculations both diffusion coefficient and kinematic viscosity were taken from literature data: $D=0.36\ 10^{-9}\ m^2/s$ [6.14], $\nu=2.61\ 10^{-6}\ m^2/s$ (calculated from η [6.15] and ρ).

A plate and frame module was assumed, with a length of L=0.5 m and a channel height of H=0.5 cm; the hydraulic diameter $d_h=2.H=0.01$ m. The Schmidt number is $Sc=\nu/D=7200$.

The mass transfer coefficients k are calculated according to Wiley et al [6.12]:

$Sh = k.d_h/D = 1.62\ Re^{0.33}\ Sc^{0.33}\ (d_h/L)^{0.33}$ *laminar flow:* $Re<2000$; $L>0.029.Re.d_h$

$Sh = k.d_h/D = 0.0096\ Re^{0.91}\ Sc^{0.35}$ *turbulent flow:* $Re>2000$; $Sc>1000$

From these equations is can be calculated that in the *laminar* flow regime mass transfer coefficients range from k=1.4 10^{-6} m/s for Re=100 till k=3.7 10^{-6} m/s for Re=2000. If the flow is *turbulent* higher mass transfer coefficients are obtained: k=7.9 10^{-6} m/s for Re=2000 and k=1.8 10^{-5} m/s for Re=5000.

A detailed survey of mass transfer relations is given by Gekas et al [6.13].

Summary

In this thesis the dehydration of ethanol/water mixtures by pervaporation using homogeneous membranes is studied. Both the general transport mechanism as well as the development of highly selective membranes for ethanol/water separation are investigated.

The ultimate goal in the development of membranes for the separation of liquid mixtures by pervaporation is to obtain a membrane that combines a high selectivity towards a mixture together with a high flux. Because pervaporation makes use of non-porous membranes, the most important factor that determines the membrane properties is the polymer material. The flux and selectivity of these membranes are determined by the physico-chemical nature of the liquid components and of the polymer membrane material. A solution-diffusion model can be used to describe transport through these membranes. According to this model, components from the feed are transported through the membrane, according to three consecutive steps:
i) *sorption* of the components into the membrane, at the feed side;
ii) *diffusion* through the membrane, due to an activity gradient;
iii) *desorption* into the vapour phase, at the permeate side.
Whereas it is generally assumed that diffusion is the rate-determining step, differences in solubility (preferential sorption) are believed to be the main factor determining the overall selectivity during pervaporation. Hence, the transport properties of pervaporation membranes can be described if the diffusivities and solubilities of the permeating components in the polymer material are known. Although this model can be used properly when permeation of pure components is considered, the permeation of liquid mixtures is far more complicated. The main problem in the latter case is that the components do not absorb and diffuse independently in the membrane: due to mutual interactions between the two components, sorption and diffusion phenomena of binary liquid mixtures during pervaporation are difficult to predict. Furthermore, once a polymer is chosen, the properties of the actual membrane applied in a practical situation are affected by a great number of other factors. Some of these are the membrane preparation method and pretreatment, the presence of additional transport resistances or the process conditions.

Still, the solution-diffusion model is a good starting point for the choice of the polymer material for a given separation problem. If during pervaporation equilibrium sorption of the components into the membrane is assumed, the equilibrium sorption selectivity can give an indication of the selectivity during pervaporation. High pervaporation selectivities can be expected when a high preferential sorption of the components in the polymer material takes place.

To study the influence of different aspects on the pervaporation properties of homogeneous membranes for the dehydration of ethanol/water mixtures, such as preferential sorption, membrane preparation method and feed conditions, two polymers are selected: poly(vinylalcohol)

(PVA) and poly(acrylonitrile) (PAN).

PVA membranes are known for its good pervaporation properties for the dehydration of ethanol/water mixtures. The pervaporation and equilibrium sorption properties of homogeneous PVA membranes with respect to ethanol/water mixtures are studied at 25°C, and described in chapter 2. For all feed concentrations water is absorbed preferentially, and water also permeates preferentially through these membranes. A high equilibrium sorption selectivity for water is found for ethanol-rich feed concentrations, but it strongly decreases with increasing water content in the feed. Because the pervaporation selectivity does not show the same trend, it is concluded that also selective diffusion of ethanol/water mixtures contributes to some extent to the overall separation in pervaporation.

The properties of PVA membranes can be influenced by applying a heat-treatment (leading to an increase in crystallinity) or by crosslinking. In chapter 2 the effect of crosslinking and crystallinity on the preferential sorption of liquid mixtures in non-porous membranes is considered theoretically, and demonstrated by some numerical examples. It is concluded that due to crosslinking of an amorphous polymer, or due to crystallinity in a semi-crystalline polymer, the equilibrium sorption properties are influenced. With increasing crosslinking density or increased crystallinity the total sorption of a liquid mixture in a polymer decreases, and the preferential sorption increases.

In chapter 3 the influence of the crystallinity of PVA membranes on the dehydration of ethanol/water mixtures is studied, by varying the degree of hydrolysis of PVA or by applying a heat-treatment. The permeation results are compared with results from equilibrium sorption experiments. High equilibrium sorption selectivities and pervaporation selectivities are obtained, caused by the low solubility and low permeability of ethanol, respectively. Ethanol only absorbs and permeates in these membranes due to the presence and permeation of water, respectively. A heat-treatment generally increases the crystallinity of the membranes, which results in an increased pervaporation selectivity and a lower flux. By crosslinking the membranes with maleic acid, higher fluxes are obtained compared to membranes without maleic acid, while the selectivity remains about the same.

Another polymer that is studied, in chapter 4, is poly(acrylonitrile) (PAN). Homogeneous PAN membranes show extremely high selectivities for the dehydration of ethanol/water mixtures by pervaporation, but the fluxes are very low. According to the solution-diffusion model fluxes through homogeneous membranes can be increased by decreasing the membrane thickness, without loss of selectivity. By decreasing the membrane thickness of these membranes, indeed higher experimental fluxes are obtained, but the selectivity decreases strongly, especially for very thin membranes. It is found that these lower selectivities for thin membranes are mainly due to a less dense membrane structure, compared to thick membranes. By influencing the evaporation rate of the solvent from a casted film the selectivities of the membranes can be influenced significantly.

The main reason for low fluxes of ethanol/water mixtures through many polymeric membranes is the low absorption in these membranes. The overall sorption can be increased by blending these polymers with water-soluble polymers. By blending highly selective PAN or poly(sulfone) (PSf) with poly(vinylpyrrolidone) (PVP) or poly(maleicanhydride) (PMA), as is studied in chapter 5, the fluxes through these membranes could be increased strongly, but generally only at the expense of the selectivity. In some cases a synergistic effect is found: at low PVP or PMA content in the PAN blend membranes both the flux and selectivity are increased. Although no spectacular improvements are obtained in the overall membrane performance, the main advantage of using blend membranes is that the permeation properties can be adjusted to a desired level.

Finally, in chapter 6 the effect of concentration polarization on pervaporation results is studied, using numerical examples. It is shown that in most situations concentration polarization generally can be avoided in pervaporation, when the feed flow conditions are turbulent. In the case of laminar flow, concentration polarization can lead to a decrease of both flux and selectivity. These effects observed are strongest at high fluxes, especially at high selectivities or at low concentrations of the preferentially permeating component in the feed.

Samenvatting

In dit proefschrift wordt de ontwatering van ethanol/water mengsels door pervaporatie m.b.v. homogene membranen beschreven. Zowel het algemene transportmechanisme voor pervaporatie als de ontwikkeling van zeer selectieve membranen voor ethanol/water mengsels zijn bestudeerd.

Het uiteindelijke doel van membraanontwikkeling voor de scheiding van vloeistofmengsels door pervaporatie is een membraan dat zowel een hoge selectiviteit als een hoge flux heeft. Omdat voor pervaporatie niet-poreuze membranen worden gebruikt, is het polymeer(materiaal) de belangrijkste factor die de membraaneigenschappen bepaalt. De flux en selectiviteit van membranen wordt bepaald door de fysisch-chemische eigenschappen van het polymeer en van de permeërende componenten. Transport door deze membranen kan worden beschreven met het oplos-diffusie model. Volgens dit model vindt transport van de componenten uit de voeding door het membraan plaats volgens de volgende drie stappen:

i) *sorptie* van de componenten in het membraan, aan de voedingszijde;
ii) *diffusie* door het membraan, als gevolg van een activiteitengradient;
iii) *desorptie* in een dampfase, aan de permeaatzijde.

In het algemeen wordt aangenomen dat de diffusie-stap de snelheidsbepalende stap is in het mechanisme, terwijl verschillen in oplosbaarheid van de componenten in het polymeer (preferentiële sorptie) voor een groot deel de uiteindelijke scheiding tijdens pervaporatie bepalen. De transporteigenschappen van pervaporatiemembranen kunnen worden beschreven als de diffusie- en sorptie-eigenschappen van de permeërende componenten in het polymere materiaal bekend zijn. Hoewel dit model goed kan worden toegepast voor permeatie van zuivere vloeistoffen, de permeatie van vloeistofmengsels is veel gecompliceerder. Het probleem is dat de componenten niet onafhankelijk in het membraan worden opgenomen of diffunderen. Als gevolg van onderlinge beïnvloeding tussen de twee componenten kunnen de sorptie en diffusie van een binair vloeistofmengsel moeilijk worden voorspeld. Bovendien worden de eigenschappen van een membraan van een gekozen polymeer beïnvloed door een groot aantal andere factoren, zoals de bereidingsmethode en voorbehandeling van het membraan, de aanwezigheid van extra transportweerstanden of de procescondities.

Toch is het oplos-diffusie model een goed startpunt voor de keuze van een polymeer materiaal voor een specifiek scheidingsprobleem. Als wordt aangenomen dat de sorptie van de componenten aan de voedingszijde van een membraan een evenwicht is, kan de evenwichtssorptie-selectiviteit een goede maat zijn voor de te verwachten pervaporatie-selectiviteit. Hoge pervaporatie-selectiviteiten kunnen worden verwacht als er een grote preferentiële sorptie plaats vindt in het polymeer.

Om de invloed van diverse aspecten op de pervaporatie-eigenschappen van homogene membranen voor de ontwatering van ethanol/water mengsels te onderzoeken, zoals preferentiële sorptie, membraan bereidingsmethode en voedingscondities, zijn twee polymeren gekozen: poly(vinylalcohol) (PVA) and poly(acrylonitril) (PAN).

PVA membranen zijn bekend voor hun goede pervaporatie-eigenschappen voor de ontwatering van ethanol/water mengsels. De eigenschappen van homogene PVA membranen m.b.t. pervaporatie en evenwichtssorptie zijn bepaald voor ethanol/water mengsels bij 25°C, en zijn beschreven in hoofdstuk 2. Voor alle voedingssamenstellingen wordt water preferentiëel opgenomen, en water permeëert ook preferentiëel door deze membranen. Een hoge evenwichtssorptie-selectiviteit voor water is gevonden voor hoge ethanol concentraties, maar deze neemt sterk af met toenemende water concentratie in de voeding. Omdat de pervaporatie-selectiviteit niet dezelfde trend vertoont, wordt geconcludeerd dat selectieve diffusie van ethanol/water mengsels ook bijdraagt in de totale scheiding tijdens pervaporatie.

De eigenschappen van PVA membranen kunnen worden beïnvloed door een warmtebehandeling (verhoging van de kristalliniteit) of door crosslinking. In hoofdstuk 2 is het effect van crosslinking en kristalliniteit op de preferentiële sorptie van vloeistofmengsels in niet-poreuze membranen theoretisch behandeld. Aan de hand van enkele numerieke voorbeelden is aangetoond dat door crosslinking van een amorf polymeer de evenwichtssorptie-eigenschappen worden beinvloed. Met toenemende crosslinkdichtheid of toenemende kristalliniteit neemt de totale sorptie van een vloeistofmengsel af, terwijl de preferentiële sorptie toeneemt.

In hoofdstuk 3 is de invloed van de kristalliniteit van PVA membranen op de ontwatering van ethanol/water mengsels bestudeerd, door variatie van de hydrolysegraad van PVA of door een warmtebehandeling toe te passen. De permeatieresultaten zijn vergeleken met de resultaten van evenwichtssorptie-experimenten. Hoge sorptie-selectivteiten en pervaporatie-selectiviteiten zijn verkregen, veroorzaakt door respectievelijk de lage sorptie en de lage permeabiliteit van ethanol. Ethanol wordt alleen opgenomen en permeëert alleen in de membranen door respectievelijk de aanwezigheid en de permeatie van water. Een warmtebehandeling verhoogt in het algemeen de kristalliniteit van de membranen, hetgeen leidt tot een hogere pervaporatie-selectiviteit en een lagere flux. Door crosslinking van de membranen met maleïnezuur worden hogere fluxen verkregen in vergelijking tot de membranen zonder maleïnezuur, terwijl de selectiviteit ongeveer gelijk blijft.

Een ander polymeer dat is bestudeerd, in hoofdstuk 4, is poly(acrylonitril) (PAN). Homogene PAN membranen hebben extreem hoge pervaporatie-selectiviteiten voor de ontwatering van ethanol/water mengsels, maar de fluxen zijn erg laag. Volgens het oplos-diffusie model kunnen de fluxen door homogene membranen worden verhoogd door de membraandikte te verlagen, bij gelijkblijvende selectiviteit. Door dunnere membranen te gebruiken zijn inderdaad hogere experimentele fluxen bereikt, maar de selectiviteit neemt sterk af, vooral voor erg dunne membranen.

Het is gebleken dat deze lage selectiviteiten vooral een gevolg zijn van een minder dichte membraanstructuur, vergeleken met dikke membranen. Door de verdampingssnelheid van het oplosmiddel van een gestreken film te variëren kan de selectiviteit sterk worden beïnvloed.

De voornaamste oorzaak voor de lage fluxen van ethanol/water mengsels voor veel polymere membranen is de lage absorptie in deze membranen. De totale sorptie kan worden verhoogd door deze polymeren te blenden met water-oplosbare polymeren. Door het blenden van het zeer selectieve PAN of poly(sulfon) (PSf) met poly(vinylpyrrolidon) (PVP) of poly(maleïne anhydride) (PMA), konden de fluxen sterk worden verhoogd, maar alleen ten koste van de selectiviteit (hoofdstuk 5). In een aantal gevallen wordt een synergetisch effect gevonden: voor laag gehalte PVP of PMA in membranen van PAN blends worden zowel de flux als de selectiviteit verhoogd. Hoewel geen spectaculaire verbeteringen zijn bereikt in de overall membraaneigenschappen, is het voordeel van blend membranen dat de permeatie-eigenschappen eenvoudig kunnen worden beïnvloed.

Tenslotte, in hoofdstuk 6 is het effect van concentratie polarisatie op pervaporatieresultaten bestudeerd d.m.v. numerieke voorbeelden. Het blijkt dat in de meeste gevallen concentratie polarisatie kan worden voorkomen tijdens pervaporatie, als de stromingscondities in de voeding turbulent zijn. Voor laminaire stroming kan concentratie polarisatie leiden tot een verlaging van zowel de flux als de selectiviteit. Deze effecten zijn het grootst voor hoge fluxen, vooral bij hoge selectiviteiten of bij lage concentraties van de preferentiëel permeërende component in de voeding.

Levensloop

Jos Spitzen werd geboren op 6 juni 1959 te Meppel. Aan de Rijksscholengemeenschap "J.H. Tromp Meesters" te Steenwijk werd in 1976 het HAVO diploma en in 1978 het Atheneum-B diploma behaald. In 1978 begon hij met de studie Chemische Technologie aan de toenmalige Technische Hogeschool Twente (nu Universiteit Twente) te Enschede. Na in 1982 het kandidaats-diploma behaald te hebben werd in 1984 de studie afgerond met het ingenieurs-diploma. Het afstudeeronderzoek werd verricht in de vakgroep Procestechniek onder leiding van prof. ir. drs. J. Groot Wassink en handelde over een modelbeschrijving van een pervaporatieproces voor de ontwatering van ethanol. In juli 1984 trad hij in dienst van de T.H. Twente als wetenschappelijk assistent in de werkgroep Membraanfiltratie van de afdeling Chemische Technologie, onder leiding van prof. dr. C.A. Smolders. In de periode tot 1 juli 1988 is onderzoek verricht dat in dit proefschrift is beschreven.

Vanaf 15 september 1988 is hij als research medewerker in dienst van Dow Chemical (Nederland) BV te Terneuzen.