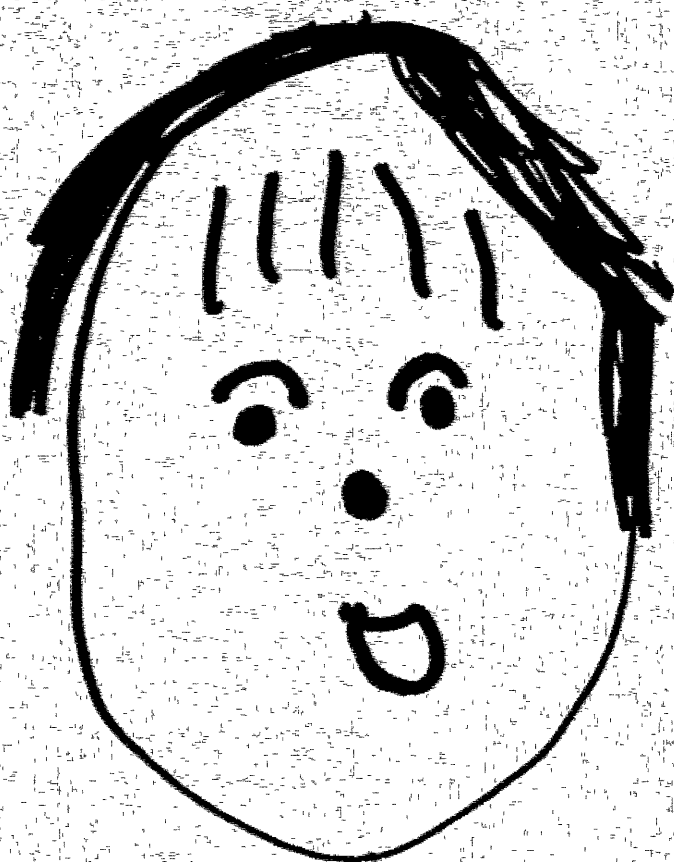# SEPARATION OF ALCOHOLS
FROM ORGANIC LIQUID MIXTURES
BY PERVAPORATION

Hyun-Chae Park

24

SEPARATION OF ALCOHOLS FROM ORGANIC LIQUID MIXTURES BY PERVAPORATION

PROEFSCHRIFT

ter verkrijging van
de graad van doctor aan de Universiteit Twente,
op gezag van de rector magnificus,
prof. dr. Th.J.A. Popma,
volgens besluit van het College van Dekanen
in het openbaar te verdedigen
op donderdag 7 januari 1993 te 15.00 uur

door

Hyun-Chae Park

geboren op 29 december 1959
te Kimhae, Korea

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

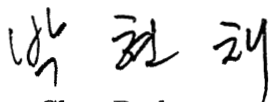*To Hye-Jin, So-Yun and Jae-Wan*

(Papa by So-Yun)

PREFACE

My four year study at the 'Universiteit Twente' ends up with this thesis. The last four years were very valuable to my academic experience. It seems even more valuable for me to see and understand a bit of the daily life of Europeans. I am very grateful to Prof. C.A. Smolders and Marcel Mulder for giving me an opportunity to study here, and also for their kind supervision of my research work.

I was very lucky that I had good colleagues and room mates. They helped me very much and I'd like to thank them for their help. Especially Robert Meertens. I'd like to thank him very much, more than very much, for his help, both private and experimental. Niels Ramaker also added up much on the chapter 5 of this thesis. I also express my special thanks to my room mates Geert-Henk, Harry, Petrus, Gert, Matthias, Richard, Ingo, Erik and Emile for their kind help and discussion; probably they sometimes got tired on translating Dutch to English for me. And equally to all other people, particularly the 'Klaverjassen' partners, Zandrie, Herman, etc.

My best thanks go to my wife Hye-Jin and my lovely kids So-Yun and Jae-Wan as well. The last four year period was a very hard time for her. The only thing she could do was 'being patient'. Everything here was new and strange to her and it was very difficult for her to find close friends. I also appreciate my parents very much for their kind support by encouraging me.

Finally I as well as my family would like to express our special thanks to Prof. and Mrs. Smolders. We enjoyed Christmas parties at their home, special home-made cookies, etc. The same thanks to Marcel and his wife. They were very helpful in making arrangements for our flat and furniture. Furthermore when I as well as my family had any problem Marcel was always a good discussion partner.

박 현 채

Hyun-Chae Park

CONTENTS

**Chapter 3.   Pervaporation of Alcohol–Toluene Mixtures through
                 Polymer Blend Membranes of Poly(Acrylic Acid) and
                 Poly(Vinyl Alcohol)**

**Chapter 4.   Sorption of Alcohol–Toluene Mixtures in PAA–PVA
                 Blend Membranes and Its Role on Pervaporation**

Chapter 5.   Separation of MTBE–Methanol Mixtures by Pervaporation

Chapter *1*

INTRODUCTION

1. Liquid mixture separation in the chemical industry

In the chemical industry, in the pharmaceutical industry, and in a number of other industries separation processes are necessary to separate and purify products and raw materials [1,2]. Separation processes are also widely used in other applications such as in recycling valuable materials from waste streams.

Unit operations for separation processes can be classified in phase separation techniques and component separation techniques based on the nature of the feed mixtures to be separated. The former techniques are used for the separation of heterogeneous mixtures, in which the feed is already present in two or more separated phases on a micro-scale. The latter are suitable for the separation of homogeneous mixtures such as gaseous mixtures and mixtures of completely miscible liquids. In these cases the separation into individual components is generally achieved by utilizing the differences in physico-chemical properties of components, and is much more difficult compared to phase separation techniques. Separation processes such as distillation, evaporation, liquid-liquid extraction, and crystallization belong to this class.

For the separation of a homogeneous liquid mixture in the chemical industry, distillation is generally the preferred technique [3,4]. The basic principle in distillation is the difference in composition between a liquid phase and a vapor phase. The composition difference between two phases is due to differences in vapor pressures, or volatilities, of the components of the liquid mixture. In this process thermal energy is the driving force for separation. No additives are required here, which might cause a

pollution problem of the final products or generate a need for an extra separation step to avoid this problem. The simplicity in operation is another advantage of this technique. However an adequate separation can not be performed by conventional distillation if the volatility differences are very small or do not exist at all. This is the case with close-boiling hydrocarbons, azeotropic mixtures, and various isomers. The separation of these mixtures is nowadays performed by other, generally energy-consuming, processes like extractive or azeotropic distillation and liquid-liquid extraction.

2. Pervaporation as an alternative separation technique

The characteristic of distillation is the requirement of energy in the form of heat to accomplish a separation, and this can represent a significant cost factor. It is estimated that 40 % of the total energy consumed by the chemical processing industry is used in distillation operations. Especially since the Arab oil embargo in 1973 which caused a rapid increase in energy costs, there has been an emphasis on energy-efficient separation methods. Existing separation methods have been reviewed in terms of energy efficiency, and also there have been research efforts in developing new separation techniques with a low energy consumption. One outcome of this search is the membrane separation process. Membrane processes offer good prospects since the energy consumption is generally much lower compared to the conventional separation methods.

Pervaporation is a membrane process which can be used to separate liquid mixtures. In this process a semi-permeable membrane through which permeation occurs separates the pervaporation unit into two parts. At the upstream compartment the liquid mixture to be separated is brought into direct contact with the membrane. The permeated product is removed as a vapor phase at the other compartment by applying a low partial vapor pressure usually by means of vacuum or a carrier gas.

For the separation of liquid mixtures pervaporation can replace all distillation units in the chemical processing industries. But this option is not economically feasible for most applications. In pervaporation a part of the processed liquid mixture (the permeate) undergoes a phase change from liquid to vapor during transport through the membrane. Therefore

the heat of vaporization of the permeate must be supplied. From this point of view pervaporation might not offer so much benefit over the conventional distillation techniques. However pervaporation is very attractive in removing minor components from liquid mixtures for purification or recovery purposes. This is definitely the case for the separation of azeotropic and close-boiling mixtures. Therefore the best utilization of pervaporation can be made by integrating this membrane process with distillation in a hybrid system, where pervaporation is used to replace energy-intensive separation techniques such as azeotropic distillation and liquid-liquid extraction.

Until now a number of studies have been reported to integrate pervaporation with distillation, particularly for the dehydration of organic solvents. In such cases the comparison of production cost has been performed to illustrate the advantage of the pervaporation process. Recently, for example, Pearce has carried out a study to compare the cost of production of 99 and 99.9 wt.% ethanol by distillation starting from a 50 wt.% ethanol feed mixture with water [5]. The separation costs were evaluated for two procedures: conventional distillation technology and distillation combined with pervaporation by using a composite membrane produced by Kalsep, UK. In the former case the normal distillation was used to produce the azeotrope, which was subsequently broken with a benzene entrainer. In the latter case the feed was dehydrated to an optimum sub-azeotropic composition of 92.6 wt.% ethanol by distillation. This product was then further dehydrated by pervaporation to 99 or 99.9 wt.% ethanol. From his study it was concluded that a hybrid system combining distillation with pervaporation could reduce the overall production cost for 99 wt.% ethanol by more than 30 %, with energy savings of 60 %. In the production of 99.9 wt.% ethanol the production cost could be reduced by 10 %. Besides the above mentioned example, there have been many other studies comparing the production cost of organic solvents [6-9]. All the cost comparisons have shown that pervaporation is far more economical than the conventional separation techniques in removing the last small amounts of water from the organic solvents. Thus pervaporation is nowadays accepted as a unit operation in the chemical industry for this application: the dehydration of organic solvents.

3. Liquid mixture separation by pervaporation

The pervaporation process is a potential option for the separation of liquid mixtures. In principle this process can be applied to separate all kinds of organic liquid mixtures in the chemical industry. It can also be used in other areas such as the concentration of heat-sensitive products in the pharmaceutical and food industries and the removal of volatile organic contaminants from waste water. Such possible applications can be classified as intermediates in between aqueous and non-aqueous mixtures. The former category includes liquid mixtures containing water as one component, while the latter refers to organic-organic mixtures.

3.1. Separation of aqueous mixtures

The pervaporation application in the separation of aqueous mixtures can be represented by the dehydration of organic solvents [10-13]. A well known example is the dehydration of ethyl alcohol. The aqueous solution of ethanol has satisfied human needs for a beverage for thousands of years. It also has been used as solvent and medicine. In addition, there is an increasing interest in anhydrous ethanol as motor fuel produced by fermentation of biomass. Distillation techniques are widely used to concentrate the fermentation ethanol. In order to obtain anhydrous ethanol, an additional separation step is necessary because of an azeotropic composition at 4.43 wt.% water at 760 mmHg. Azeotropic or extractive distillation are generally used for this purpose. However the high energy consumption and operational complexity of these processes make pervaporation optional as an alternative. In this case pervaporation can be used to break the azeotrope and to remove the last part of the water presence in ethanol. During the last two decades this area has been studied intensively. As a result pervaporation is now applied for the dehydration of organic solvents on technical scales with capacities of up to 120,000 l of 99.8 % ethanol/day [12,13].

Besides the dehydration purpose, pervaporation can also be used to remove organic solvents from their dilute aqueous solutions [14,15]. Alcohols can be removed from fermentation broths, and traces of volatile organic contaminants can be removed from waste water. The pervaporation application in this area is expected to reach the commercial stage in the near future.

3.2. Separation of organic-organic mixtures

In the chemical and petro-chemical industries the separation of organic-organic mixtures is a major separation problem. In measures of bulk quantity it is much more important than the aqueous systems. In the early 1960s when systematic studies on pervaporation were started, the separation of non-aqueous liquid mixtures was a major target to solve. Binning and his colleagues carried out a series of investigations for the separation of hydrocarbon mixtures [16-18]. Since then a number of studies have been reported in this area. Despite these research efforts the commercial application of pervaporation for the separation of organic-organic mixtures is still in an embryonic stage. This is mainly due to the fact that membranes developed for this purpose have shown rather unsatisfactory results. Also the lack of membrane modules which can withstand the relatively severe conditions required for this separation is hindering the commercial application of pervaporation in this sector.

In recent years, however, the pervaporation process for this separation area is actively studied. This is partially encouraged by the successful application of pervaporation in dehydrating organic solvents. Separation problems related to newly emerging processes in the chemical industry, recycling of organics, and more severe restrictions on environmental protection are also stimulating the use of pervaporation. If problems associated with membrane and module stability can be solved, the organic-organic mixture separation by pervaporation will be a major membrane application around the year 2000 [19].

4. Survey of pervaporation research in organic/organic separation

The separation of organic-organic mixtures is potentially a major application area of pervaporation in the chemical processing industries. The number of possible applications is very large. It may be roughly classified as follows:

— separation of polar/non-polar solvent mixtures
— separation of aromatic/aliphatic mixtures
— separation of aliphatic hydrocarbons
— separation of aromatic isomers

The research which is carried out until now is surveyed and discussed following the classification given above.

4.1. Separation of polar/non-polar solvent mixtures

Interactions between polymeric membranes and penetrants play an important role in liquid separation. If there is a large difference in chemical nature between mixture components, a satisfactory separation will be obtained by using polymer membranes which interact preferentially with one of the mixture components. This is the case with polar/non-polar solvent mixtures. This type of mixture was intensively studied by Aptel et al. by using poly(tetrafluoro ethylene) membranes grafted with Lewis base groups: poly(N-vinyl pyrrolidone) [20-22] and poly(4-vinyl pyridine) [20,23] (table 1). Because a Lewis base is a proton-acceptor, the membranes can possess nucleophilic groups. It implies that these membranes can preferentially interact with electrophilic molecules such as alcohols, but not with non-polar hydrocarbons. With these membranes a number of liquid mixtures have been tested for pervaporation. The component of a mixture which is able to form hydrogen bonds with the polymer showed a higher permeation rate than the other component. The best separation was obtained for the azeotropic mixtures of alcohols with aliphatic hydrocarbons; for instance, a selectivity value of 24 for the azeotrope of propanol and cyclohexane. And relatively good selectivities were observed for the chloroform/hydrocarbon systems. In contrast, the azeotropic mixtures of the type alcohol/ester, alcohol/ketone, and carboxylic acid/pyridine showed a poor separation performance. This may be due to the hydrogen bonding ability between the components of these mixtures. Moreover it appeared that the weak interaction force between the hydroxyl functionality of an aliphatic alcohol with the π electrons of an aromatic ring was sufficient to hinder the efficiency of separation of aliphatic alcohol/aromatic hydrocarbon mixtures by these grafted membranes.

Besides the above mentioned studies, a number of investigations have been reported which were mainly applied to the pervaporation of mixtures of aliphatic alcohols with hydrocarbons (table 2). From these investigations it was observed that generally polar molecules permeated faster through polar membranes than non-polar molecules, and vice

versa. Polar polymers such as poly(vinyl alcohol), Nafion, and cellulose acetate were found to be selectively permeable for alcohols over hydrocarbons. But aliphatic and aromatic hydrocarbons always permeated preferentially through polyethylene, polypropylene and natural rubber with respect to alcohols.

Table 1. Pervaporation through poly(tetrafluoro ethylene) (PTFE) membranes grafted with Lewis base.

Membrane	Liquid mixture

PTFE grafted with poly(*N*-vinyl pyrrolidone) [20-22]

methanol/benzene, methanol/acetone, methanol/methyl acetate, methanol/ethyl acetate, methanol/methyl acrylate,

ethanol/hexane, ethanol/cyclohexane, ethanol/benzene, ethanol/toluene, ethanol/chloroform, ethanol/1,2-dichloroethane, ethanol/ethyl acetate, ethanol/ethyl acrylate, ethanol/triethylamine,

propanol/cyclohexane, propanol/benzene, propanol/diethyl ketone, iso-propanol/cyclohexane, iso-propanol/ethyl acetate,

butanol/cyclohexane, butanol/pyridine,

acetic acid/1,2-dichloroethane, acetic acid/dioxane, acetic acid/pyridine, acetic acid/*N,N*-dimethyl formamide, formic acid/pyridine, propionic acid/pyridine,

chloroform/pentane, chloroform/hexane, chloroform/cyclohexane, chloroform/benzene, chloroform/acetone, chloroform/methyl ethyl ketone

PTFE grafted with poly(4-vinyl pyridine) [20, 23]

chloroform/pentane, chloroform/hexane, chloroform/cyclohexane, chloroform/ethyl ether

Table 2. Pervaporation of polar/non-polar solvent mixtures.

Liquid mixture	Membrane material

 methanol/aliphatic hydrocarbon

       poly(vinyl alcohol) [24, 25]; poly(phenylene oxide) [26]; Nafion* [24, 26];

       polyether sulphone [24]; blend of poly(acrylic acid) with Nylon 6 [24, 27];

       alloy of phosphonate polymer with cellulose acetate [26];

 methanol/aromatic hydrocarbon

       cellulose triacetate [16]; polyethylene [16, 28, 29]; polypropylene [29];

       Nitrile rubber [30]; perfluorosulfonic acid [31]

 methanol/methyl *tert*-butyl ether

       cellulose acetate [32, 33]; Nafion [24, 34]; poly(vinyl alcohol) [34];

       cellulose base material MT [24]

 methanol/dimethyl carbonate

       Nafion [34]; poly(vinyl alcohol) [34, 35]

 ethanol/aliphatic hydrocarbon

       poly(vinyl alcohol) [25]; cellulose acetate [36, 37]; cellophane [37, 41];

       perfluorosulfonic acid [31]; poly(hexamethylene adipamide) [36];

       polyethylene, polypropylene, and rubber hydrochloride [37];

       polyester, natural rubber, ethylene–vinyl acetate copolymer,

       ethyl acrylate–chloroethylvinyl ether copolymer,

       and natural rubber–methyl methacrylate graft copolymer [38]

 ethanol/aromatic hydrocarbon

       polyethylene [39]; polyphenylquinoxaline [40];

       perfluorosulfonic acid [31]; natural rubber and polyester [38];

 iso-propanol/hydrocarbon

       poly(vinyl alcohol) [25]; perfluorosulfonic acid [31];

       polyethylene [28, 42]; polypropylene [43]

 butanol/toluene

       polypropylene [44]

(continued)

Table 2. (continued)

aromatic alcohol/benzene
      polyethylene and modified polyethylene [45]

acetic acid/aromatic hydrocarbon
      polypropylene [43]

acetone/hexane
      polyethylene, polypropylene, poly(vinyl chloride), cellophane,
      and vinylidene chloride–vinyl chloride copolymer [37]

aniline/benzene
      polyethylene and modified polyethylene [45]

* Nafion: copolymer of polysulfonyl fluoride vinyl ether and poly(tetrafluoro
  ethylene)

4.2. Separation of aromatic/aliphatic mixtures

The mixture of benzene with cyclohexane is a representative of this class of liquid mixtures. The difference in boiling points between benzene and cyclohexane is only 0.6 °C. The vapor liquid equilibrium curve of this mixture shows the typical feature of close-boiling mixture system. Furthermore they form an azeotrope at 52.2 wt.% benzene. This means that it is very difficult to separate by conventional separation techniques such as distillation. Therefore much attention has been given to the separation by pervaporation (table 3).

Commercially available polymers were first tested as membrane materials, and new polymers were carefully designed and tested for this separation problem. For all membranes reported in published works, benzene permeated preferentially over cyclohexane, but to a different extent. For a 1/1 by wt mixture, high fluxes were obtained by using polyethylene and polypropylene, but selectivities were very low, less than 2. On the other hand, polar membranes such as cellulose acetate and cellulose acetate butyrate showed higher selectivities although fluxes were much lower than in the case of polyethylene and polypropylene. Some new polymeric materials were finely designed for the separation

of this mixture. These include graft copolymer of methacrylate with 2-hydroxyethyl methacrylate, copolymer of 2-hydroxy-3-(diethylamine) propyl methacrylate with styrene, and alloys of phosphonate and

Table 3. Pervaporation of aromatic/aliphatic liquid mixtures.

Liquid mixture	Membrane material
benzene/ cyclohexane	polyethylene [29, 46-48]; polypropylene [29, 43, 48, 49]; Neoprene rubber [30]; polyphenylquinoxaline [40]; cellulose ester and ether [25]; cellulose acetate [26]; cellulose acetate butyrate and modified cellulose acetate butyrate [18, 50]; poly(γ-methyl L-glutamate) [51]; poly(bis(2,2,2-trifluoroethoxy)phosphazene) [52]; modified poly(vinylidene fluoride) [53, 54]; graft copolymer of methacrylate and 2-hydroxyethyl methacrylate [55]; ethylene–carboxylic acid copolymer [48]; copolymer of 2-hydroxy-3-(diethylamine)propyl methacrylate with styrene [56]; alloys of phosphonate and phosphate polymers with cellulose acetate [26, 57-59]
benzene/ other paraffins	NBR and SBR [62]; polyethylene [43, 47, 60, 61]; polyethylene grafted with polystyrene [61]; cellulose acetate butyrate [63]; Membrane F XII [25]; ethylene–carboxylic acid copolymer [48]
benzene/olefins	alloy of phosphonate polymer with cellulose acetate [58]
toluene/paraffins	Neoprene rubber [30]; polyethylene [61, 64, 65]; polyethylene grafted with polystyrene [61]; polyurethane [67]; modified poly(vinylidene fluoride) [53]; cellulose acetate butyrate [63, 66]; cellulose ester and ether [25]; ethyl cellulose [66]; modified ethyl cellulose [18]
ethyl benzene/ ethyl cyclohexane	modified poly(vinylidene fluoride) [53]

phosphate polymers with cellulose acetate. These new membranes showed a large enhancement both in permeation rate and selectivity.

Because of the very similar physical properties of benzene and cyclohexane, a low selectivity was obtained through chemically inert membranes such as polyethylene and polypropylene. However both components exhibit different chemical properties. Benzene, the principal representative of aromatic hydrocarbons, has π electrons which to a certain extent endows benzene with hydrogen bonding ability and polarity. However cyclohexane is totally non-polar. Therefore higher separation factors could be achieved through polar polymer membranes than through non-polar ones. Furthermore specific membranes could be designed based on the difference in properties like the one mentioned.

Pervaporation was also investigated for the separation of other aromatic/aliphatic hydrocarbon mixtures (table 3). In all cases reported the aromatic hydrocarbon permeated faster than the aliphatic hydrocarbon, but low selectivities were obtained.

4.3. Separation of aliphatic hydrocarbons

This type of mixture consists of molecules being very similar in chemical nature. For instance, in the case of a hexane/heptane mixture there is no apparent difference in the nature and strength of interactions between a membrane and individual permeants. Therefore permselectivity is largely governed by the steric effects of permeants: diffusional cross section and molecular length. A survey of pervaporation studies for this class of liquid mixtures is given in table 4.

In the pervaporation of the binary mixtures of paraffins, the component with the smaller molecular weight permeates faster than the other one because of a smaller diffusional cross section. In the case of methyl cyclohexane/iso-octane mixture, however, methyl cyclohexane permeates preferentially although it has a larger diffusional cross section. This discrepancy may be caused by the abnormally long molecular length of iso-octane compared with cyclohexane. This suggests that diffusion occurs by a snake-like motion preferentially along the direction of the greatest length of permeating molecule.

In the binary mixtures of olefins with paraffins, however, there is a relatively large difference in chemical nature of both components. Therefore good separation results may be expected if there is any specifically designed membrane material. This had been proved by copolymerizing 2-hydroxy-3-(diethylamine)propyl methacrylate with styrene. This copolymer was highly selective for olefins over paraffins. For instance, a complete rejection of cyclohexane was observed in the pervaporation of cyclohexene/cyclohexane mixture.

Table 4. Pervaporation of mixtures of aliphatic hydrocarbons.

Membrane material	Liquid mixture
polyethylene	hexane/heptane [39, 68]; hexane/octane [43]; hexane/neohexane [47]; cyclohexane/heptane [64]; cyclohexane/neohexane [47]; heptane/iso-octane [69]
polypropylene	heptane/iso-octane [69]
cellulose acetate butyrate [63]	3-methyl pentane/2,3-dimethyl pentane, heptane/iso-octane, methyl cyclohexane/iso-octane, 1-hexene/hexane, 2-heptene/heptane, cyclohexene/cyclohexane
ethyl cellulose and modified ethyl cellulose	heptane/iso-octane [18, 70]; methyl cyclohexane/iso-octane [18]
cellulose ester and ether [25]	hexane/iso-octane, hexene/hexane
alloy of phosphonate polymer with cellulose acetate [26]	cyclohexene/cyclohexane
P(AA-St)* [56]	cyclohexene/cyclohexane
NBR [71, 72]	1,3-butadiene/iso-butene
aromatic polyimide [73]	1,3-butadiene/trans-2-butene

* P(AA-St): copolymer of 2-hydroxy-3-(diethylamine)propyl methacrylate with styrene

4.4. Separation of aromatic isomers

This class of mixtures is one of the most difficult to separate. The industrial separation of C_8-aromatics (o-xylene, m-xylene, p-xylene and ethyl benzene) is now performed by super-fractionation, fractional crystallization, adsorption, or a combination of these methods. These processes are very complex and, in general, energy intensive. Therefore this mixture system has been considered as one of the most interesting mixtures for which the pervaporation process could be applied, and many investigations have been reported (table 5 and 6).

Pervaporation separation through commercially available polymeric films and polymers was first carried out, and new polymers such as polymer alloys were synthesized and tested. As was expected, the separation was very poor because of very similar size, shape and chemical nature of the aromatic isomers. Although xylene isomers have almost the same molecular volume, all tested membranes showed the order of selective permeation of p-xylene > m-xylene > o-xylene. This is consistent with the order of decreasing diffusional cross-section area

Table 5. Pervaporation of aromatic C_8 isomers through commercial polymer films [74].

Liquid mixture:
p-xylene/o-xylene, p-xylene/m-xylene, p-xylene/ethyl benzene
Membrane:
Polyethylene, 125A101, DuPont
Polypropylene, Clysar® 350P-1A3, DuPont
Saran Wrap®, Dow
Teflon® FEP, 200A, DuPont
Polyimide, Kapton®, 100H, DuPont
Poly(vinyl fluoride), Tedlar®, 100AG30UT, DuPont
Parylene C and N, Union Carbide
Cellulose acetate, 100CA-43, DuPont
Nylon, Allied Chemical, Capron® 77C
Poly(vinylidene fluoride), Kynar®, Pennwalt

Table 6. Pervaporation of aromatic isomers.

Liquid mixture	Membrane
C$_8$–isomers*	polyethylene [75, 76]; cellulose tripropionate and cellulose acetate butyrate [77]; Methocel HG† [80]; modified poly(vinylidene fluoride) [78]; P(HEA-HEMA)‡ and modified P(HEA-HEMA) [79];
dichlorobenzene isomers	Methocel HG† [80]
nitrochlorobenzene isomers	Methocel HG† [80]
nitrotoluene isomers	Methocel HG† [80]
benzene/toluene	poly(ethylene terephthalate) [81]
toluene/o-xylene	Nitrile rubber [30]
styrene/ethyl benzene	ethylene–carboxylic acid copolymer [48]; alloy of phosphonate polymer with cellulose acetate, poly(phenylene oxide), and Nafion [26]

* binary or ternary mixtures of *o*-, *m*-, and *p*-xylene and ethyl benzene

† hydroxypropylmetyl cellulose membranes containing Schardinger cyclodextrin

‡ copolymer of 2-hydroxyethyl acrylate and 2-hydroxyethyl methacrylate

of these isomers [75]. However polymers containing specific functional groups showed a different order of permeation rate. The order of permeation rate of *m*-xylene > *o*-xylene > *p*-xylene was observed through membranes prepared from a copolymer of 2-hydroxyethyl acrylate with 2-hydroxyethyl methacrylate modified by 3,4- or 3,5-dinitrobenzoyl chloride.

5. Structure of the thesis

The main objective of research described in this thesis is the development of new pervaporation membrane materials suitable for the separation of polar/non-polar liquid mixtures, particularly aimed on the

selective removal of alcohols from their mixtures with aromatics and ethers. In order to investigate the relation of membrane material and the separation performance, the effect of chemical interactions of penetrant-penetrant and penetrant-membrane is studied with respect to the transport mechanism.

In chapter 2 potential polymers have been selected for comparing the separation performance towards the mixtures studied. Since the aim is to remove selectively the polar alcohols from the non-polar species, only polar polymers have been chosen. The separation performance of these polymers has been evaluated by the pervaporation of ethanol-toluene mixtures.

In chapter 3 the polymer blend concept is studied with respect to the development of pervaporation membrane materials for alcohol-toluene liquid mixtures. Poly(acrylic acid) is chosen due to its very high solubility for the alcohols. To improve permselectivity and mechanical stability, poly(vinyl alcohol) has been chosen as the second polymer. This polymer showed very high permselectivities for alcohols over hydrocarbons [25].

In chapter 4 the solution part of the solution-diffusion mechanism is described. The overall sorption and the preferential sorption of methanol-toluene and ethanol-toluene liquid mixtures in the blends of poly(acrylic acid) and poly(vinyl alcohol) are determined and compared with the pervaporation results. In addition, the preferential sorption is predicted by a model which is derived from Flory-Huggins thermodynamics.

In chapter 5 the separation of methanol from methyl *tert*-butyl ether by pervaporation is discussed. Methyl *tert*-butyl ether is produced by a reaction of methanol with iso-butene. Because this is an equilibrium reaction, methanol is fed in excess up to about 20 % of the stoichiometric amount into the reactor in order to improve the conversions. The excess of methanol in the effluent exhibits a difficult separation problem in the conventional distillation process since it forms an azeotrope with methyl *tert*-butyl ether. This separation problem can be accomplished by the incorporation of a pervaporation unit.

REFERENCES

1. C. Judson King, *Separation Processes*, 2nd ed., McGraw Hill, New York (1980).

2. R.W. Rousseau (ed.), *Handbook of Separation Process Technology*, John Wiley & Sons, New York (1987).

3. M. van Winkle, *Distillation*, McGraw-Hill, New York (1967).

4. J.R. Fair, "Distillation" in: *Handbook of Separation Process Technology*, ed. by R.W. Rousseau, John Wiley & Sons, New York (1987). pp. 229-339

5. G.K. Pearce, Proc. of 4th Int'l. Conf. on Pervapor. Processes in the Chem. Ind., Ft. Lauderdale, Florida, Dec. 1989. pp. 278-296

6. U. Sander and P. Soukup, *J. Memb. Sci.*, 36 (1988) 463-475.

7. P.O. Cogat, Proc. of 3rd Int'l. Conf. on Pervapor. Processes in the Chem. Ind., Nancy, France, Sept. 1988. pp. 305-316

8. J.G.A. Bitter, ibid. pp. 476-485

9. J. Bergdorf, Proc. of 5th Int'l. Conf. on Pervapor. Processes in the Chem. Ind., Heidelberg, Germany, March 1991. pp. 362-382

10. J.W.F. Spitzen, E. Elsinghorst, M.H.V. Mulder, and C.A. Smolders, Proc. of 2nd Int'l. Conf. on Pervapor. Processes in the Chem. Ind., San Antonio, Texas, March 1987. pp. 209-224

11. M. Wesslein, A. Heintz, and R.N. Lichtenthaler, *J. Memb. Sci.*, 51 (1990) 169-179.

12. J. Néel, "Introduction to Pervaporation" in: *Pervaporation Membrane Separation Processes*, ed. by R.Y.M. Huang, Elsevier, Amsterdam (1991). pp. 1-109

13. T. Asada, "Pervaporation Membrane Plant, Industrial Experience and Plant Design in Japan", ibid. pp. 491-507

14. H.H. Nijhuis, M.H.V. Mulder, and C.A. Smolders, Proc. of 3rd Int'l. Conf. on Pervapor. Processes in the Chem. Ind., Nancy, France, Sept. 1988. pp. 239-251.

15. K.W. Böddeker and G. Bengtson, "Selective Pervaporation of Organics from Water" in: *Pervaporation Membrane Separation Processes*, ed. by R.Y.M. Huang, Elsevier, Amsterdam (1991). pp. 437-460

16. R.C. Binning and R.J. Lee, U.S. Pat. 2,953,502 (1960); and British Pat. 856,371 (1960).

17. R.C. Binning, R.J. Lee, J.F. Jennings, and E.C. Martin, *Ind. Eng. Chem.*, 53(1) (1961) 45-50.

18. E.C. Martin, R.C. Binning, L.M. Adams, and R.J. Lee, U.S. Pat. 3,140,256 (1964).

19. R.W. Baker, "Pervaporation" in: *Membrane Separation Systems – A Research & Development Needs Assessment*, Vol. 2, DOE Report No. DOE/ER/30133-H1, NTIS, Springfield, USA (1990).

20. P. Aptel, J. Cuny, J. Jozefonwicz, G. Morel, and J. Néel, *J. Appl. Polym. Sci.*, 18 (1974) 351-364.

21. P. Aptel, N. Challard, J. Cuny, and J. Néel, *J. Memb. Sci.*, 1 (1976) 271-287.

22. P. Aptel, J. Cuny, J. Jozefowicz, G. Morel, J. Néel, and B. Chaufer, *Eur. Polym. J.*, 14 (1978) 595-599.

23. P. Aptel, J. Cuny, J. Jozefowicz, G. Morel, and J. Néel, *J. Appl. Polym. Sci.*, 16 (1972) 1061-1076.

24. B.A. Farnand and S.H. Noh, *AIChE Symp. Ser.*, 85(272) (1989) 89-92.

25. W.H. Schneider, Proc. of 2nd Int'l. Conf. on Pervapor. Processes in the Chem. Ind., San Antonio, Texas, March 1987. pp. 169-175

26. I. Cabasso, *Ind. Eng. Chem. Prod. Res. Dev.*, 22 (1983) 313-319.

27. R.Y.M. Huang, M. Balakrishnan, and J-W. Rhim, Proc. of 3rd Int'l. Conf. on Pervapor. Processes in the Chem. Ind., Nancy, France, Sept. 1988. pp. 212-221

28. J.W. Carter and B. Jagannadhaswamy, *Brit. Chem. Eng.*, 9(8) (1964) 523-526.

29. E. Nagy, J. Stelmaszek, and A. Ujhidy, "Separation of Benzene-Methanol and Benzene-Cyclohexane Mixtures by Pervaporation Process", in: *Membranes and Membrane Processes*, ed. by E. Drioli and M. Nakagaki, Plenum Press, New York (1986). pp. 563-571

30. N. Vahdat, H. Taylor, and A. Alsayegh, *J. Appl. Polym. Sci.*, 44 (1992) 1233-1243.

31. B.K. Dutta and S.K. Sikdar, *AIChE J.*, 37(4) (1991) 581-588.

32. M.S. Chen, R.M. Eng, J.L. Glazer, and C.G. Wensley, US Pat. 4,774,365 (1988).

33. M.S.K. Chen, G.S. Markiewicz, and K.G. Venugopal, *AIChE Symp. Ser.*, 85(272) (1989) 82-88.

34. M. Pasternak, C.R. Bartels, and J. Reale, Jr., US Pat. 4,798,674 (1989).

35. V.M. Shah, C.R. Bartels, M. Pasternak, and J. Reale, *AIChE Symp. Ser.*, 85(272) (1989) 93-97.

36. M. Laatikainen and M. Lindström, "Separation of Methanol–Ethanol and Ethanol–n-Heptane Mixtures by Reverse Osmosis and Pervaporation", Acta Polytechnica Scandinavica, Chem. Technol. and Metallurgy Ser. No. 175, Helsinki (1986).

37. R.F. Sweeny and A. Rose, *Ind. Eng. Chem. Prod. Res. Dev.*, 4(4) (1965) 248-251.

38. H. Seradarian and S. Palu, *Revue Generale de Caoutchoucs et Plastiques*, 53(562) (1976) 55-60.

39. K.F. Knight, A. Duggal, R.A. Shelden, and E.V. Thompson, *J. Memb. Sci.*, 26 (1986) 31-50.

40. G. Chen, F. Lu, B. Wu, Y. Shi, S. Zhang, and C. Zhang, Proc. of 3rd Int'l. Conf. on Pervapor. Processes in the Chem. Ind., Nancy, France, Sept. 1988. pp. 188-193

41. C. Castellari, *Atti Della Academia Ligure di Scienze e Lettere*, 33 (1977) 166-178.

42. J.W. Carter and B. Jagannadhaswamy, Proc. of Symp. on the Less Common Means of Separation, Birmingham, April 1963. pp. 35-42

43. J.I. Dytnerski, "Membranprozesse zur Trennung flüssiger Gemische", VEB. Deutsche Verlag für Grundstoffenindustrie, Leipzig, Germany (1977).

44. J.I. Dytnerski and W.N. Golowin, *Chem. Techn.*, 6 (1966) 334-339.

45. S. Yamada and T. Hamaya, *J. Memb. Sci.*, 17 (1984) 125-138.

46. R. Rautenbach and R. Albrecht, *J. Memb. Sci.*, 7 (1980) 203-223.

47. R.Y.M. Huang and V.J.C. Lin, *J. Appl. Polym. Sci.*, 12 (1968) 2615-2631.

48. M. Hirata, T. Ishikawa, S.Kobayashi, N. Ito, and T.Yoshida, Japan Pat. 77,111,888 (1977).

49. M. Kucharski and J. Stelmaszek, *Intern. Chem. Eng.*, 7(4) (1967) 618-622.

50. E.C. Martin and J.T. Kelly, US Pat. 2,981,730 (1961).

51. F. Suzuki and K. Onozato, *J. Appl. Polym. Sci.*, 27 (1982) 4229-4238.

52. F. Suzuki, K. Onozato, H. Yaegashi, and T. Masuko, *J. Appl. Polym. Sci.*, 34 (1987) 2197-2204.

53. F.P. McCandless, *Ind. Eng. Chem. Proc. Des. Dev.*, 12(3) (1973) 354-359.

54. F.P. McCandless, D.P. Alzheimer, and R.B. Hartman, *Ind. Eng. Chem. Proc. Des. Dev.*, 13(3) (1974) 310-312.

55. J. Terada, T. Hohjoh, S. Yoshimasu, M. Ikemi, and I. Shinohara, *Polym. J.*, 14(5) (1982) 347-353.

56. S. Yoshimasu, H. Nomura, K. Komiya, T. Okano, and I. Shinohara, *Nippon Kagaku Kaishi*, (1980) 1785-1791.

57. I. Cabasso, J. Jagur-Grodzinski, and D. Vofsi, *J. Appl. Polym. Sci.*, 18 (1974) 2117-2136.

58. I. Cabasso, J. Jagur-Grodzinski, and D. Vofsi, *J. Appl. Polym. Sci.*, 18 (1974) 2137-2147.

59. H.R. Acharya, S.A. Stern, Z.Z. Liu, and I. Cabasso, *J. Memb. Sci.*, 37 (1988) 205-232.

60. M. Fels and R.Y.M. Huang, *J. Macromol. Sci. - Phys.*, B5(1) (1971) 89-110.

61. R.Y.M. Huang and M. Fels, *Chem. Eng. Prog.; Symp. Ser.*, 65(91) (1969) 52-58.

62. C. Larchet, J.P. Brun, and M. Guillou, *J. Memb. Sci.*, 15 (1983) 81-96.

63. J.M. Stuckey, US Pat. 2,930,754 (1960).

64. M. Fels, *AIChE Symp. Ser.*, 68(120) (1972) 49-57.

65. S.K. Ghosh and B.S. Rawat, *Indian J. Technol. Short Commun.*, 4 (1966) 62-64.

66. J.M. Stuckey, US Pat. 3,043, 891 (1962).

67. H. Ohst, K. Hildenbrand, and R. Dhein, Proc. of 5th Int'l. Conf. on Pervapor. Processes in the Chem. Ind., Heidelberg, Germany, March 1991. pp. 7-21

68. F.W. Greenlaw, R.A. Shelden, and E.V. Thompson, *J. Memb. Sci.*, 2 (1977) 333-348.

69. J.G.A. Bitter, *Desalination*, 51 (1984) 19-35.

70. J.M. Stuckey, US Pat. 2,958,656 (1960).

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

72. J.P. Brun, G. Bulvestre, A. Kergreis, and M. Guillou, *J. Appl. Polym. Sci.*, 18 (1974) 1663-1683.

73. E. Perry and W.F. Strazik, US Pat. 3,789,079 (1974).

74. F.P. McCandless and W.B. Downs, *J. Memb. Sci.*, 30 (1987) 111-116.

75. A.S. Michaels, R.F. Baddour, H.J. Bixler, and C.Y. Choo, *Ind. Eng. Chem. Proc. Des. Dev.*, 1 (1962) 14-25.

76. M. Wessling, U. Werner, and S.-T. Hwang, *J. Memb. Sci.*, 57 (1991) 257-270.

77. M.H.V. Mulder, F. Kruitz, and C.A. Smolders, *J. Memb. Sci.*, 11 (1982) 349-363.

78. J.G. Sikonia and F.P. McCandless, *J. Memb. Sci.*, 4 (1978) 229-241.

79. K. Ishihara, K. Matsui, H. Fujii, H. Nishide, and I. Shinohara, *Chem. Letters*, (1985) 1663-1666.

80. C.H. Lee, *J. Appl. Polym. Sci.*, 26 (1981) 489-497.

81. F. Suzuki, K. Onozato, and N. Takahashi, *J. Appl. Polym. Sci.*, 27 (1982) 2179-2188.

PERVAPORATION OF
POLAR–NONPOLAR LIQUID MIXTURES

— MEMBRANE MATERIAL SCREENING

Summary

The pervaporation process can be applied to separate all kinds of polar/nonpolar organic mixtures. To accomplish a wide field of application, a more systematic study seems to be necessary, particularly focussed on developing proper membrane materials.

Ethanol–toluene was chosen as a model mixture for the material screening. Comparison of the physical properties of ethanol and toluene showed that the difference in polarity and hydrogen bonding ability seemed to be the most significant ones. Based on these characteristics a number of commercially available polar polymers were selected and tested for their separation behavior. These polymers contain functional groups which can form hydrogen bonds with alcohols.

Among membranes made by single polymers cellulose type of materials showed a good pervaporation performance. In order to improve the permselectivity of materials the concept of polymer blending was used. From the pervaporation experiments it was observed that polymer blending could give optimal membranes for this type of separation.

1. INTRODUCTION

Special interest for the pervaporation process to replace distillation for the separation of organic mixtures in the chemical processing industries is mainly caused by a reduced energy consumption and equipment cost. Some liquid mixtures such as azeotropic mixtures, close-boiling hydrocarbons, and various isomers are difficult to separate by a simple distillation technique. Often other energy-consuming processes like azeotropic distillation, pressure distillation and liquid-liquid extraction are used. The relatively high energy consumption for these processes has encouraged the development of new, less energy-consuming separation processes such as pervaporation.

Binning and his coworkers were pioneers in studying the pervaporation process [1-3]. In the early 1960s, they investigated the separation of various mixtures, especially the separation of hydrocarbons which were of interest for the petro-chemical industry. Some commercially available polymers and polymer films were also tested by Carter et al. [4,5] and Sweeny et al. [6]. Since then a number of pervaporation studies have been reported. Nowadays the pervaporation process has been accepted as a unit operation in the chemical industry for the dehydration of organic solvents. This can be visualized by the number of commercial plants which have been installed [7,8]. However the large-scale separation of organic-organic mixtures is still in an embryonic stage. This is mainly due to the lack of good membrane materials. Membranes tested so far for the separation of organic-organic mixtures by pervaporation have shown rather unsatisfactory results to compete with other existing separation techniques. Therefore a lot of research effort is still focussed on the development of new membrane materials for specific separation problems.

In the case of pervaporation the permeation of molecules through a membrane is generally described by a solution-diffusion mechanism [9]. According to this model the permselectivity of a membrane towards a binary mixture is determined by the differences in either solubility or diffusivity of the components in the membrane. Until now especially the solubility term has been studied extensively for material screening.

The solubility of a solute in a polymer is strongly related to the mutual interaction. Three different approaches have been proposed to correlate the separation properties of a membrane with the interactions between

the permeating molecules and the membrane.

— three-dimensional solubility parameter approach [10-14]
— surface thermodynamic approach [13-15]
— Dimroth's solvent polarity value [16-19]

These methods are helpful as a first estimate of interaction phenomena between permeating molecules and membrane materials, and can be used as a qualitative guide for the material selection.

In this study the three-dimensional solubility parameter approach has been used to select feasible polymer materials. The interaction between a permeating molecule and a membrane, which is directly related to the solubility of a penetrant in a membrane, can be described qualitatively by means of the solubility parameter theory. The three component solubility parameter can be considered as a vector lying in a three dimensional (δ_d, δ_p, δ_h)–space. Each solvent and each polymer can be located in this three dimensional space being the end-point of the radius vector. For a binary system consisting of a polymer and a solvent, the distance Δ_{12} between the end-points of the radius-vectors can be expressed as [20]:

$$\Delta_{12} = [(\delta_{d,1} - \delta_{d,2})^2 + (\delta_{p,1} - \delta_{p,2})^2 + (\delta_{h,1} - \delta_{h,2})^2]^{1/2} \tag{1}$$

where subscripts 1 and 2 denote polymer and solvent, respectively. Subscripts d, p, and h refer to dispersive, polar, and hydrogen bonding forces, respectively. This Δ_{12} is a measure for the affinity between penetrant and polymer, and a very simple and a useful parameter to obtain qualitative information on interaction phenomena. When Δ_{12} decreases, the affinity between penetrant and polymer increases, and in this way polymers may be selected.

Our investigations were particularly aimed to separate polar solvents from nonpolar ones. The mixtures of low molecular weight aliphatic alcohols with toluene were chosen as a model mixture system. For the selective removal of alcohols by pervaporation, the membrane materials must preferentially interact with the alcohols. Therefore polymers which are polar and can form hydrogen bonds with alcohols were selected. This may result in a preferential sorption of alcohols over toluene due to the

polar-polar and hydrogen bonding interactions with alcohols. The separation ability of these polymers for ethanol-toluene mixtures was evaluated.

2. EXPERIMENTAL

2.1. Materials

Ethyl alcohol and toluene (analytical grade) were obtained from Merck Co. The polymers used in this study are summarized in table 1 together with their suppliers and solvents used for preparing the homogeneous membranes. All chemicals were used without any further purification. Water was demineralized before use.

2.2. Membrane preparation

Membrane casting solutions were prepared by dissolving polymers in proper solvents. In the case of a two-component polymer blend membrane, both component polymers were first separately dissolved in a common solvent, and then the resulting two solutions were mixed together in various proportions to obtain the proper composition. Homogeneous membranes were prepared by casting a polymer solution on a Perspex plate or a glass plate with a casting knife. The solvent was slowly removed by evaporation in a flowing nitrogen atmosphere at room temperature. The thickness of resulting homogeneous membranes was approximately 20 μm.

2.3. Pervaporation experiments

The pervaporation experiments were performed on a laboratory test apparatus, which is schematically represented in figure 1. Membranes were installed in stainless steel pervaporation cells. The effective membrane area in each cell was 28 cm^2. The feed was circulated through the cells from a feed reservoir at a constant temperature. The pressure at the downstream side was kept below 5 mmHg by a vacuum pump. The

permeate was collected in cold traps cooled by liquid nitrogen, and analyzed by gas chromatography equipped with a thermal conductivity detector.

The pervaporation properties are characterized by the pervaporation flux J and the pervaporation selectivity α_p. Fluxes were determined by measuring the weight of liquid collected in the cold traps during a certain

Table 1. Polymers and their suppliers.

polymer	Mw (g/mol)	casting solvent*	supplier
Poly(vinyl alcohol)			
100% hydrolyzed	115,000	water	Aldrich Chemical
96% hydrolyzed	85,000~146,000	water	Aldrich Chemical
88% hydrolyzed	80,000~100,000	water	Aldrich Chemical
Poly(acrylonitrile)		DMF	Aldrich Chemical
Poly(acrylic acid)	250,000	water	Aldrich Chemical
Poly(acryl amide)	~5,500,000	water	Aldrich Chemical
Poly(acryl amide), carboxyl modified			
low carboxyl content	200,000	water	Aldrich Chemical
high carboxyl content	200,000	water	Aldrich Chemical
Poly(vinyl acetate)	33,000	DMF	British Drug Houses
Poly(methyl methacrylate)	medium Mw	chloroform	Aldrich Chemical
Poly(N-vinyl pyrrolidone)	360,000	water	Janssen Chimica
Cellulose acetate (acetyl 39.8 %)	30,000	acetone	Aldrich Chemical
Cellulose triacetate		chloroform	Aldrich Chemical
Cellulose nitrate		acetone	Polyscience
Cellulose propionate	200,000	DCE	Aldrich Chemical
Ethylene–vinyl alcohol copolymer			
of 56 mol % vinyl alcohol content		DMAc	Polyscience
Clarene L4[†]	90,000	DMAc	Solvay
Clarene R20[†]	50,000	DMAc	Solvay
Levapren 400[‡]		chloroform	Bayer

* DMF: dimethyl formamide; DCE: dichloroethane; DMAc: dimethyl acetamide

[†] Clarene: ethylene–vinyl alcohol copolymer

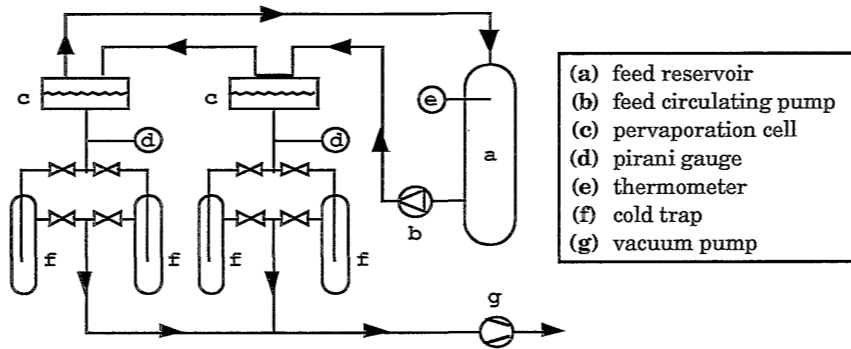[‡] Levapren: ethylene–vinyl acetate copolymer

Figure 1. Schematic representation of a laboratory test apparatus for the pervaporation experiments.

time at steady state conditions. The fluxes of different membranes were normalized to a membrane thickness of 20 μm, assuming a proportionality between the flux and the reciprocal membrane thickness. The pervaporation selectivity α_P is defined by:

$$\alpha_P = (y_1/y_2) / (x_1/x_2) \qquad (2)$$

where x and y represent the concentration in the feed and in the permeate, respectively. Indices 1 and 2 refer respectively to the more permeable component, ethanol in this study, and the less permeable one, toluene.

3. RESULTS AND DISCUSSION

3.1. Selection of membrane material

In the case of liquid separation there is generally a strong interaction between penetrants and the polymeric membrane. The performance of a membrane is very much dependent on the properties of the feed mixture to be separated. Binning et al. [2] have already pointed out that the molecular shape factor of penetrants will govern the permselectivity of the pervaporation process when the difference in chemical nature of the

penetrants is not large. However, when the difference in chemical nature or solubility character is very large, the interaction of the specific penetrants with the polymer will determine predominantly the permeability properties. Size and shape factors may have very little influence on the permeability in that case. Therefore the physical and chemical properties of solvents to be investigated may give some information for the first selection of membrane materials.

Our investigations were particularly aimed to separate low molecular weight alcohols from nonpolar solvents such as benzene, toluene, and methyl *tert*-butyl ether. Some physical properties of these chemicals are given in table 2. As the two groups of organics, alcohols and nonpolar solvents, are compared, the differences in polarity and hydrogen bonding ability is very significant. For example, the solubility parameter value of ethanol due to hydrogen bonding forces, δ_h, is about 10 times higher than that of toluene. The molecular size is also quite different and may affect the separation as well. The molar volumes of methanol or ethanol are about half of those of toluene or methyl *tert*-butyl ether. Therefore it is

Table 2. Physical properties of solvents.

solvent	Mw	molar volume†	bp	vapor pressure‡	solubility parameter			
					δ	δ_d	δ_p	δ_h
	(g/mol)	(cm^3/mol)	(°C)	(mmHg)	(cal$^{1/2}$/cm$^{3/2}$)			
Methanol	32.04	40.7	65.2	164.0	14.5	7.4	6.0	10.9
Ethanol	46.07	58.7	78.5	78.4	13.0	7.7	4.3	9.5
Propanol	60.11	75.2	97.4	28.3	12.0	7.8	3.3	8.5
Butanol	74.12	92.0	117.2	9.3	11.3	7.8	2.8	7.7
Benzene	78.12	89.4	80.1	119.3	9.1	9.0	0.0	1.0
Toluene	92.15	106.9	110.6	36.7	8.9	8.8	0.7	1.0
MTBE*	88.15	119.0	55.2	306.6	8.1	7.6	1.7	2.4

* Solubility parameters of MTBE (methyl *tert*-butyl ether): calculated by the group contribution method proposed by Hoftyzer and van Krevelen [21]

† at 25 °C

‡ at 30 °C

expected that polar polymers possessing hydrogen bonding ability will show a much better affinity for alcohols than for the nonpolar solvents like toluene, resulting in high permselectivity for alcohols. This constituted the basis for our first choice of polymeric materials.

3.2. Pervaporation of ethanol-toluene liquid mixture

First some commercially available polar polymers were chosen and their pervaporation characteristics were investigated by using an ethanol-toluene (1/1 by wt) liquid mixture. The pervaporation measurements were conducted at 30 °C. Results are given in table 3. Some polymers such as 100 % hydrolyzed poly(vinyl alcohol) or polyacrylonitrile showed extremely low fluxes. It was practically impossible to collect a large enough quantity of permeate to analyze the results accurately by gas chromatography. Only the 88 % hydrolyzed poly(vinyl alcohol) showed a measurable flux of 22.4 g/m^2h, but the selectivity was rather low being 4.0 for ethanol. Some other polymers, such as poly(acrylic acid) or poly(N-vinyl pyrrolidone), were too highly swollen or dissolved in an ethanol-toluene (1/1 by wt) mixture. Therefore it was impossible to carry out pervaporation experiments for these materials. Membranes made of poly(acryl amide) and carboxyl modified poly(acryl amide) with low and high carboxyl contents were very brittle in a dry state; i.e., it was not possible to use them in a thin film form. Therefore these polymers were omitted from the pervaporation test. Although poly(vinyl acetate) and poly(methyl methacrylate) contain a hydrogen bonding functionality, an ester group, and are classified as polar polymers, they dissolved in toluene. This means that they may not be preferentially permeable for alcohols, or, if so, then the pervaporation selectivity may be very low. Another polymer with an ester linkage is Levapren 400 which is an ethylene–vinyl acetate copolymer with a vinyl acetate content of 40 %. This polymer was selective for toluene with the selectivity value for toluene of 4.0.

Cellulosic type materials seem to be good candidates for the selective permeation of alcohols due to their hydrophilic character. They are widely used as a reverse osmosis membrane material for the desalination of brackish water. Some of these materials were subjected to the pervaporation test. The results are given in table 4. Cellulose acetate, cellulose triacetate, and cellulose nitrate showed high flux values of 310 to

1350 g/m^{2}h, and all were preferentially permeable for ethanol. However, the selectivity values for ethanol over toluene were very low; in the range of 1.3 to 2.6. Cellulose propionate showed a two times higher solubility of toluene over ethanol. This means that this polymer membrane might be preferentially permeable for toluene.

Collagen has a similar molecular structure as cellulosic materials. Therefore it may be also a good candidate for the selective pervaporation of alcohols. Collagen membranes, both uncrosslinked and crosslinked, were obtained from Naturin-Werk Becker & Co., Weinheim, Germany, and tested without any further treatment. They showed rather good separation characteristics (table 4). Although the fluxes were lower, the selectivity values were almost one order of magnitude higher compared to the cellulosic membranes.

Table 3. Pervaporation of an ethanol-toluene (1 / 1 by wt) mixture at 30 °C using commercial polymers with a polar character.

membrane	flux[†] (g/m^{2}h)	$\alpha_{EtOH/Toluene}$
Poly(vinyl alcohol)		
100% hydrolyzed	@	—
96% hydrolyzed	@	—
88% hydrolyzed	22.4	4.0
Levapren 400[‡]	4000	0.25
Poly(acrylonitrile)	@	—
Poly(acrylic acid)	too highly swollen in the feed mixture	
Poly(acryl amide)	too brittle	
Poly(acryl amide), carboxyl modified		
low carboxyl content	too brittle	
high carboxyl content	too highly swollen in the feed mixture	
Poly(vinyl acetate)	dissolves in toluene	
Poly(methyl methacrylate)	dissolves in toluene	
Poly(N-vinyl pyrrolidone)	dissolves in the feed mixture	

† flux normalized to a membrane thickness of 20 μm

‡ crosslinked with dicumyl peroxide (4 wt.%)

@ insufficient amount of permeate to be analyzed

Table 4. Pervaporation of an ethanol-toluene (1 / 1 by wt) mixture through cellulose type polymers and through Collagen membranes.

membrane	temperature (°C)	flux* (g/m²h)	$\alpha_{EtOH/Toluene}$
Cellulose acetate	30	186	3.4
	30	314	2.3
	30	310	2.6
	30	183	3.4
Cellulose triacetate	30	602	1.6
	30	597	1.7
	30	656	1.3
Cellulose nitrate	30	1350	1.9
Cellulose propionate	two times higher toluene solubility than ethanol		
Collagen membrane			
uncrosslinked	30	80	28.4
	30	73	36.0
	40	156	20.7
crosslinked	30	27	11.7
	40	58	24.0

* flux normalized to a membrane thickness of 20 μm

Polymers with a sulfonyl group are also hydrophilic and are able to form hydrogen bonds. In the case of ultrafiltration and microfiltration, the sulfonation of polymers like polysulfone was studied to increase the hydrophilicity of membranes. In this study poly(ether ether ketone) was chosen and sulfonated with concentrated sulfonic acid. The detailed experimental procedure of sulfonation is described elsewhere [22]. The degree of sulfonation, i.e., number of sulfonyl groups per repeating unit of polymer backbone, ranged from 0.5 to 0.6. The sulfonated poly(ether ether ketone) membrane with a sulfonation degree of 0.5 showed a high flux of 1.4 kg/m²h for an ethanol-toluene (1/1 by wt) liquid mixture. However the selectivity was very low, less than 3. To improve the selectivity, the membranes were sulfonated to a higher degree and crosslinked. However the obtained selectivity was still low, less than 7 (table 5).

Table 5. Pervaporation of ethanol-toluene mixtures through sulfonated poly(ether ether ketone) membranes at 30 °C.

sulfonation degree[†]	wt.% ethanol		flux[‡] (g/m^2h)	$\alpha_{EtOH/Toluene}$
	feed	permeate		
0.5	47.6	68.6	1432	2.4
		66.6	1358	2.2
		69.3	1386	2.5
		66.1	1432	2.1
0.5*	50.4	82.4	26	4.6
		82.6	21	4.7
0.6*	50.4	86.9	36	6.5

† number of sulfonyl groups per repeating unit

‡ flux normalized to a membrane thickness of 20 μm

* crosslinked with 1,4-phenylene diamine (5 wt.%)

Ethylene–vinyl alcohol copolymers possess the possibility of controlling the balance between hydrophilic and hydrophobic character by varying the ratio of ethylene and vinyl alcohol moieties. As the portion of the vinyl alcohol moiety increases, the number of hydroxyl groups increases and the copolymer becomes more hydrophilic. Therefore this class of materials might be of interest to investigate the effect of chemical interactions between permeants and membranes. Furthermore the glass transition temperatures of these copolymers are rather low. For example, the glass transition temperatures of Clarene R20 and Clarene L4, which are ethylene-vinyl alcohol copolymers with vinyl alcohol contents of 60 and 71 mol %, are 54 °C and 64 °C, respectively. In addition, in a swollen state the glass transition temperature may be even much lower. Therefore it is possible to carry out the pervaporation experiments with these polar polymer membranes in the elastomeric state. The pervaporation results are given in table 6. Ethylene–vinyl alcohol copolymer membranes of three different compositions, i.e. vinyl alcohol contents of 56, 60, and 71 mol %, respectively, were tested. All tested membranes were permselective for ethanol, and the selectivity values increased as the vinyl alcohol content increased. However the pervaporation flux decreased with increasing vinyl alcohol content. The flux of an ethanol-toluene liquid mixture (1/1 by

wt) at 30 °C decreased gradually, and reached a very low value of around 2 g/m^{2}h as the vinyl alcohol content increased up to 71 mol %. The copolymer of this composition seems to have the same flux range as a 100 % hydrolyzed poly(vinyl alcohol) which is an extreme case of the ethylene–vinyl alcohol copolymer. The total flux through all three membranes at 30 °C was very low. With increasing pervaporation temperature, however, the flux increased by almost one order of magnitude with a temperature increase of 10 °C, but the selectivity decreased.

Table 6. Pervaporation of ethanol-toluene mixtures through ethylene–vinyl alcohol copolymer membranes.

vinyl alcohol content (mol %)	T (°C)	wt.% ethanol		flux* (g/m^{2}h)	$\alpha_{EtOH/Toluene}$
		feed	permeate		
71 %[†]	30	49.3	99.9	1.1	1027.4
		49.3	99.6	1.9	256.1
		49.3	99.9	2.3	1027.4
	40	49.9	90.5	12.9	9.6
		49.9	92.3	11.5	12.0
	50	50.0	85.3	82.8	5.8
60 %[‡]	30	48.5	97.9	4.7	49.5
		48.5	93.6	3.7	15.5
		48.5	99.1	6.3	116.9
	50	50.0	78.6	281.4	3.7
56 %	30	49.9	89.8	10.8	8.8
	40	49.9	85.1	44.0	5.7
		49.9	82.2	54.3	4.6
	30	10.0	90.2	4.7	82.8

* flux normalized to a membrane thickness of 20 μm

† Clarene L4

‡ Clarene R20

3.3. Polymer blend membrane

In developing a polymeric membrane material for pervaporation, commercially available polymers and polymer films are tested first. However, the separation properties are quite often unsatisfactory. Therefore much research effort is aimed on the development of new 'tailor-made' materials by synthesis of new polymers or by modification of existing polymers. Another method is the blending of polymers. This technology is very interesting due to the low development costs and the capability to develop new membrane materials [23-27].

Polymer blends of poly(vinyl alcohol) with poly(N-vinyl pyrrolidone)

The polymer blend concept can be utilized to improve the permeation rate of a polymer membrane which is very selective for one component of a mixture to be separated but with a low permeation rate. By combining this polymer with a suitable second polymer with a higher sorption capability for the feed mixture than the former, a range of different materials with an improved permeation rate can be developed.

Poly(vinyl alcohol) is chosen as a basic selective polymer because this polymer is very selective for alcohols over hydrocarbons [28]. For example, in the separation of a liquid mixture of ethanol/n-hexane (1/9 by wt) poly(vinyl alcohol) membranes showed a permeate composition of 99 % ethanol.

The ethanol-toluene separation through the blend membranes of poly(vinyl alcohol) and poly(N-vinyl pyrrolidone) has been evaluated. The results are presented in table 7. For the blend of 88 % hydrolyzed poly(vinyl alcohol), it was observed that with increasing poly(N-vinyl pyrrolidone) content from 0 to 50 wt.% the flux of an ethanol-toluene (1/1 by wt) mixture increased exponentially from 22 to 3900 g/m^2h at 30 °C, whereas the selectivity decreased from 4 to 1 (nonselective). For the same mixture with the same composition the blend membrane of 96 % hydrolyzed poly(vinyl alcohol) showed also a drastic flux increase up to 2120 g/m^2h as the poly(N-vinyl pyrrolidone) content reached a concentration of 50 wt.%, while the membrane became also nonselective.

Table 7. Pervaporation of ethanol-toluene mixtures through membranes made from polymer blends of poly(vinyl alcohol) and poly(N-vinyl pyrrolidone) (PVP).

PVP wt.% in the blend	T (°C)	wt.% ethanol feed	wt.% ethanol permeate	flux* (g/m²h)	$\alpha_{EtOH/Toluene}$
Blend of 88 % hydrolyzed poly(vinyl alcohol)					
0	30	50.0	79.9	22	4.0
10	30	50.6	77.2	91	3.3
25	30	50.0	70.6	680	2.4
50	30	50.0	50.9	3900	1.0
Blend of 96 % hydrolyzed poly(vinyl alcohol)					
30	30	10.4	83.1	31	42.3
		10.4	84.1	35	45.6
		10.4	82.6	39	40.9
40	30	10.4	44.4	740	6.9
		10.4	45.7	699	7.3
15	30	50.8	91.2	30	10.0
		50.8	85.4	31	5.7
		50.8	89.7	33	8.4
		49.3	70.6	49	2.5
20	30	49.3	91.4	9	10.9
25	30	50.5	87.5	18	6.9
40	30	51.2	66.6	1316	1.9
		51.2	67.0	1244	1.9
50	30	50.2	49.9	2120	1.0
15	50	50.2	90.3	43	9.2
		50.2	91.9	43	11.3
20	50	50.4	86.9	81	6.5
		50.4	86.5	69	6.3

* flux normalized to a membrane thickness of 20 μm

 Polymer blends of poly(acrylic acid) with poly(vinyl alcohol)

Poly(acrylic acid) is extremely swollen in an ethanol-toluene (1/1 by wt) liquid mixture. For this reason, the pervaporation test with this pure polymer could not be performed. If the extent of swelling could be reduced, poly(acrylic acid) is expected to have a high permeation rate for alcohols such as methanol and ethanol because of the high affinity towards these alcohols.

Swelling can be reduced by means of crosslinking. Poly(acrylic acid) can easily be crosslinked by di-epoxides or metal ions. However, membranes crosslinked by these crosslinking agents were very brittle. Reduction of swelling can also be achieved by blending with other polymers which show a low sorption for the mixtures to be separated. Poly(vinyl alcohol) was chosen as the other component polymer of the blend because of its very high selectivity for alcohols over hydrocarbons [28]. Furthermore this blend membrane can easily be crosslinked covalently through an ester linkage formation between a hydroxyl group of poly(vinyl alcohol) and a carboxyl group of poly(acrylic acid).

Poly(acrylic acid) was blended in various proportions with 96 % hydrolyzed poly(vinyl alcohol). The poly(vinyl alcohol) content ranged from 10 to 35 wt.%. As it was expected, membranes made of the blend were much less swollen in ethanol-toluene liquid mixtures than in the case of pure poly(acrylic acid). The pervaporation results of these mixtures through the poly(acrylic acid)–poly(vinyl alcohol) blend membranes are presented in table 8. Ethanol permeated preferentially through all tested membranes, and the selectivity increased as the poly(vinyl alcohol) content in the blends increased. However the flux decreased with the poly(vinyl alcohol) content, which might be due to the reduction of swelling of the blends.

4. CONCLUSIONS

Some commercially available polar polymers were screened based on the difference in physical properties between ethanol and toluene. To evaluate their separation ability pervaporation tests were carried out using ethanol-toluene liquid mixtures.

Table 8. Pervaporation of ethanol-toluene mixtures through membranes made from a polymer blend of poly(acrylic acid) and 96 % hydrolyzed poly(vinyl alcohol) (PVA) at 30 °C.

PVA wt.% in the blend	wt.% ethanol feed	wt.% ethanol permeate	flux* (g/m^2h)	$\alpha_{EtOH/Toluene}$
10	10.4	96.9	28	269
	9.8	94.2	47	149
	11.6	93.9	66	117
10	50.0	95.6	510	21.7
15	49.7	97.6	680	41.2
	49.2	96.8	461	31.2
20	48.5	98.4	430	65.3
	51.4	96.9	436	29.6
	49.3	97.4	665	38.5
	49.8	97.1	688	33.8
30	50.0	97.7	292	42.5
	50.0	98.7	151	75.9
35	49.7	95.5	175	21.5
	48.9	96.9	184	32.7
	48.9	96.2	174	26.4

* flux normalized to a membrane thickness of 20 µm

From the pervaporation experiments it was generally observed that polar polymers were selectively permeable for ethanol. For instance, cellulose acetate membranes showed a selectivity range of 2.3 to 3.4 for ethanol in the pervaporation of an ethanol-toluene (1/1 by wt) mixture at 30 °C. Poly(vinyl alcohol) with a degree of hydrolysis of 88 % was selective for ethanol as well, showing a selectivity value of about 4.0 for the same mixture. However, some polymers were selective for toluene although they were considered to be polar. For example, the membrane prepared from Levapren 400, an ethylene–vinyl acetate copolymer, showed a selectivity value of 4.0 for toluene.

Polymers like poly(vinyl alcohol) and polyacrylonitrile were selected and tested because they were expected to be highly selective for ethanol.

However, they showed extremely low permeation rates for an ethanol-toluene (1/1 by wt) mixture. It was impossible to collect a minimal quantity of permeate to analyze the performance accurately. Ethylene–vinyl alcohol copolymer membranes also showed very low flux values of less than 10 g/m^2h at 30 °C. Some other polymers such as poly(acrylic acid) and poly(N-vinyl pyrrolidone) were not suitable as membrane because of extremely high swelling in the test liquid mixture. However, by blending poly(acrylic acid) with poly(vinyl alcohol) a feasible membrane material was obtained. As the poly(vinyl alcohol) content in the blend increased from 10 to 35 wt.%, the flux values decreased from 0.5 to 0.15 kg/m^2h with increasing selectivity from 22 to 76 for an ethanol-toluene (1/1 by wt) mixture. This implies that the polymer blend concept can be well utilized for the design of new membrane materials.

REFERENCES

1. R.C. Binning and R.J. Lee, U.S. Pat. 2,953,502 (1960); and British Pat. 856,371 (1960).

2. R.C. Binning, R.J. Lee, J.F. Jennings, and E.C. Martin, *Ind. Eng. Chem.*, 53(1) (1961) 45-50.

3. E.C. Martin, R.C. Binning, L.M. Adams, and R.J. Lee, U.S. Pat. 3,140,256 (1964).

4. J.W. Carter and B. Jagannadhaswamy, "Liquid Separations Using Polymer Films", Proc. of Symp. on the Less Common Means of Separation, Birmingham, April 1963. pp. 35-42

5. J.W. Carter and B. Jagannadhaswamy, *Brit. Chem. Eng.*, 9(8) (1964) 523-526.

6. R.F. Sweeny and A. Rose, *Ind. Eng. Chem. Prod. Res. Dev.*, 4(4) (1965) 248-251.

7. J. Néel, "Introduction to Pervaporation" in: *Pervaporation Membrane Separation Processes*, ed. by R.Y.M. Huang, Elsevier, Amsterdam (1991). pp. 1-109

8. T. Asada, "Pervaporation Membrane Plant, Industrial Experience and Plant Design in Japan", ibid. pp. 491-507

9. M.H.V. Mulder, "Thermodynamic Principles of Pervaporation", ibid. pp. 225-251

10. I. Cabasso, *Ind. Eng. Chem. Prod. Res. Dev.*, 22 (1983) 313-319.

11. C. Zhu, C. Yuang, J. Fried, and D. Greenberg, *Envir. Prog.*, 2 (1983) 132.

12. M.H.V. Mulder and C.A. Smolders, *Separation & Purification Methods*, 15(1) (1986) 1-19.

13. Y.M. Lee, D. Bourgeois, and G. Belfort, *J. Memb. Sci.*, 44 (1989) 161-181.

14. R.A. Sferrazza and C.H. Gooding, "Prediction of Sorption Selectivity in

Pervaporation Membranes", Proc. of 3rd Int'l. Conf. on Pervapor. Processes in the Chem. Ind., Nancy, France, Sept. 1988. pp. 54-60

15. C.J. van Oss, J. Visser, D.R. Absolom, S.N. Omenyi, and A.W. Neumann, *Adv. Colloid Interface Sci.*, 18 (1983) 133.

16. T. Shimidzu and M. Yoshikawa, *Polym. J.*, 15(2) (1983) 135-138.

17. M. Yoshikawa, H. Yokoi, K. Sanui, N. Ogata, and T. Shimidzu, *Polym. J.*, 16(8) (1984) 653-656.

18. M. Yoshikawa and N. Ogata, *J. Memb. Sci.*, 26 (1986) 107-113.

19. M. Yoshikawa, T. Yukoshi, K. Sanui, and N. Ogata, *J. Appl. Polym. Sci.*, 33 (1987) 2369-2392.

20. P.E. Froehling, D.M. Koenhen, A. Bantjes, and C.A. Smolders, *Polymer*, 17 (1976) 835-836.

21. D.W. van Krevelen, *Properties of Polymers – their correlation with chemical structure; their numerical estimation and prediction from additive group contributions*, 3rd ed., Elsevier, Amsterdam (1990). Chap. 7

22. G.H. Koops, "Dehydration of Acetic Acid by Pervaporation; Material Science Aspects", Ph.D. thesis, University of Twente, Enschede, The Netherlands (1992). pp. 141-157

23. I. Cabasso, J. Jagur-Grodzinski, and D. Vofsi, *J. Appl. Polym. Sci.*, 18 (1974) 2117-2136 and 2137-2147.

24. Q.T. Nguyen, "Polymer Blending Concept for the Preparation of Permselective Membranes (For Pervaporation)" in: *Synthetic Polymeric Membranes*, ed. by B. Sedlacek and J. Kahovec, Walter de Gruyter & Co., Berlin (1987). pp. 479-494

25. Z. Yun, M.-Y. Huang, and Y.-Y. Jiang, *Polym. Bulletin*, 20 (1988) 277-284.

26. X.P. Zhao and R.Y.M. Huang, *J. Appl. Polym. Sci.*, 41 (1990) 2133-2145.

27. E. Ruckenstein and J.S. Park, *J. Appl. Polym. Sci.*, 40 (1990) 213-220.

28. W.H. Schneider, "Purification of Anhydrous Organic Mixtures by Pervaporation", Proc. of 2nd Int'l. Conf. on Pervapor. Processes in the Chem. Ind., San Antonio, Texas, March 1987. pp. 169-175

PERVAPORATION OF ALCOHOL–TOLUENE MIXTURES THROUGH POLYMER BLEND MEMBRANES OF POLY(ACRYLIC ACID) AND POLY(VINYL ALCOHOL)

Summary

Homogeneous membranes were prepared by blending poly(acrylic acid) with poly(vinyl alcohol). These blend membranes were evaluated for the selective separation of alcohols from toluene by pervaporation. The flux and selectivity of the membranes were determined both as a function of the blend composition and of the feed mixture composition. The results showed that a polymer blending method could be very useful to develop new membranes with improved permselectivity. The pervaporation properties could be optimized by adjusting the blend composition. All the blend membranes tested showed a decrease in flux with increasing poly(vinyl alcohol) content for both methanol-toluene and ethanol-toluene liquid mixtures. The alcohols permeated preferentially through all tested blend membranes, and the selectivity values increased with increasing poly(vinyl alcohol) content.

The pervaporation characteristics of the blend membranes were also strongly influenced by the feed mixture composition. The fluxes increased exponentially with increasing alcohol concentration in the feed mixtures, whereas the selectivities decreased for both liquid mixtures.

1. INTRODUCTION

At the very early stage of pervaporation research it was recognized that this process possesses a high potential for the separation of organic liquid mixtures [1-4]. Since then much research has been carried out and reported [5,6]. Despite these studies no large-scale application for the organic-organic mixture separation in the chemical industry can be found so far. This is mainly due to the lack of good membranes for specific applications. Either the permeation rate or the selectivity were found to be too low or unsatisfactory for an economical industrial application.

Commercially available polymers and polymer films were first tested to investigate the potential as a membrane material. Because of unsatisfactory separation properties, much research effort has been aimed on the development of new 'tailor-made' materials for specific applications. Three approaches are often followed: (a) synthesis of new polymers, (b) modification of existing polymers, and (c) polymer blending. The synthesis of new polymers or copolymers is the first way to prepare 'tailor-made' materials. Based on the knowledge of permeation and separation mechanism specific membrane materials can be designed and synthesized for a given separation problem. For the pervaporation of organic liquid mixtures many new polymers and copolymers were synthesized and tested [7-10]. These polymers generally showed an improved permselectivity when they contained specific groups which could preferentially interact with one component of a liquid mixture. In recent years new polymerization techniques such as radiation grafting and plasma grafting are also studied for the development of pervaporation membranes [11-13]. The modification of polymers can be done through a chemical reaction, a radiation or plasma treatment, or a combination of these methods. In this way specific groups are introduced to the polymer bulk [14,15] or only to the surface of polymer membranes [16]. A third method is the blending of existing polymers to produce materials with new properties. It is possible to produce a range of materials with properties in between or completely different from those of the blend constituents. An obvious advantage of this polymer blending approach is the low development costs. It usually requires little or no capital expenditure in comparison with the production of new polymers. This approach has been tested for the development of membrane materials for the pervaporation of liquid mixtures, and promising results were

observed [17-21].

The objective of material study is to develop membranes with both a high flux and a high selectivity. However, in most cases a so-called 'trade-off' trend can be found. This means that as a flux increases, then a selectivity decreases, or vice versa. For this reason membrane development is often characterized by an optimization procedure: the performance of membranes has to be adjusted for a given separation problem in order to achieve an optimal performance. For this purpose a polymer blend can offer a convenient tool. The aim of polymer blending is normally to create a new polymeric material that combines the properties of two (or more) homo-polymers. In a homogeneous blend made of two polymers, the component polymers are mixed on a molecular level. In this case, the properties of the blend is generally in between those of two component polymers being related to the composition of the blend. This means that the physical and mechanical properties as well as the permeation properties of the blend can be influenced by changing the blend composition.

The main objective of this work is to develop new polymer membranes for the selective separation of alcohols from aromatic hydrocarbons by pervaporation. For this purpose a polymer blend concept was applied; in this study a blend of poly(acrylic acid) and poly(vinyl alcohol). The pervaporation property of this blend was evaluated for ethanol-toluene and methanol-toluene liquid mixtures.

2. EXPERIMENTAL

2.1. Materials

Poly(acrylic acid) (PAA) (Mw = 250,000 g/mol) and poly(vinyl alcohol) (PVA) (96% hydrolyzed, Mw = 85,000 ~ 146,000 g/mol) were purchased from Aldrich Chemical Co. Methyl alcohol, ethyl alcohol, toluene, and iso-octane (analytical grade) were obtained from Merck Co. They were used without any further purification. Water was demineralized before use.

2.2. Membrane preparation

Polymer blending was performed by a solution method. Both component polymers, poly(acrylic acid) and poly(vinyl alcohol), were separately dissolved in water. Two solutions were mixed together in various proportions to obtain the desired polymer solutions. Homogeneous membranes were prepared by casting the polymer solution on a Perspex plate with a casting knife. The solvent, water, was slowly removed by evaporation in a flowing nitrogen gas stream at room temperature. The thickness of the resulting membranes was in the range of 15 to 60 µm.

2.3. Glass transition temperature measurements

The glass transition temperature of poly(acrylic acid), poly(vinyl alcohol), and blends of these two polymers was measured calorimetrically with a Perkin Elmer Differential Scanning Calorimetry (DSC 4). The sample size ranged from 10 to 20 mg. DSC curves were recorded at a constant heating rate of 10 K/min. The temperatures at the midpoint of the heat capacity transition in the DSC curves were taken as the glass transition temperatures.

2.4. Density measurements

The density of the membranes was measured with a buoyancy technique. A well dried membrane sample was first weighed in air. Thereafter it was held in iso-octane at 22.5 °C and its weight was measured in that medium. The volume of the sample can be calculated from the weight difference of both measurements; dividing it by the density of iso-octane. From the weight in air and the volume, the density can be calculated.

2.5. Pervaporation experiments

The pervaporation experiments were performed using the same laboratory test apparatus as described in chapter 2 of this thesis.

Membranes which were immersed and swollen in the respective feed mixtures at room temperature were installed in the stainless steel pervaporation cells. The effective membrane area in each cell was 50 cm^2. The feed was circulated through the pervaporation cells from a feed reservoir kept at 30 °C. The pressure at the downstream side was kept below 2 mmHg by a vacuum pump. The permeate was collected in cold traps cooled by liquid nitrogen. The composition of the collected permeate was determined by gas chromatography equipped with a thermal conductivity detector.

The pervaporation properties are characterized by the flux J and the selectivity α_P. Fluxes were determined by measuring the weight of liquid collected in the cold traps during a certain time at steady state conditions. The fluxes of different membranes were normalized to a membrane thickness of 20 μm, assuming a proportionality between the flux and the reciprocal membrane thickness. The pervaporation selectivity α_P is defined by:

$$\alpha_P = (y_1/y_2) / (x_1/x_2) \tag{1}$$

where x and y represent the concentrations in the feed and in the permeate, respectively. Indices 1 and 2 refer to the more permeable component (methanol or ethanol in this study) and the less permeable one (toluene), respectively.

3. RESULTS AND DISCUSSION

3.1. Physical properties of the PAA–PVA blend

The properties of a polymer blend are particularly determined by the fact whether it is a homogeneous or heterogeneous blend. Although it can be argued how to characterize homogeneity, the existence of only one glass transition temperature (T_g) is often a clear indication [22]. A miscible blend of two homo-polymers shows a single T_g which is generally in between the T_g values of the individual polymers.

The polymer samples were carefully dried to remove completely the casting solvent, water. The presence of any solvent in a polymer sample can lower the measured T_g value due to a plasticizing effect. The samples were first dried by blowing dry nitrogen gas for 2~4 days at room temperature, and then dried for another day in a vacuum oven at room temperature.

The measured glass transition temperatures of poly(acrylic acid), poly(vinyl alcohol) and their blends are given in figure 1. The glass transition temperature decreases gradually from 129 °C to 84 °C with an increase of the poly(vinyl alcohol) content from 0 to 50 wt.%. Over this composition range each blend shows only one T_g value, indicating that the blend is homogeneous. This was also confirmed by the transparency of the membranes.
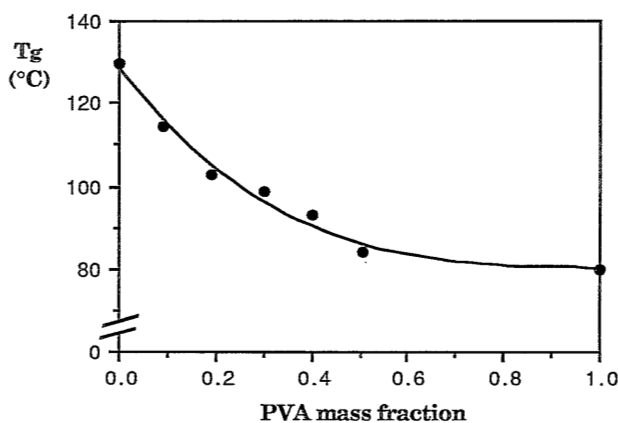
Figure 1. Glass transition temperatures (T_g) of the PAA–PVA blend as a function of the blend composition.

The density of the blends was measured to determine the presence of crystallite. Since poly(vinyl alcohol) is a semi-crystalline polymer, it may aggregate into small crystalline domains. The measured density values are plotted against the poly(vinyl alcohol) content (see figure 2). This figure shows that all measured densities are lying on a straight line connecting the densities of pure poly(acrylic acid) and amorphous

poly(vinyl alcohol). From this figure it appears that in the composition range of 10 to 50 wt.% poly(vinyl alcohol) there is no or a negligible crystalline fraction in the blends.
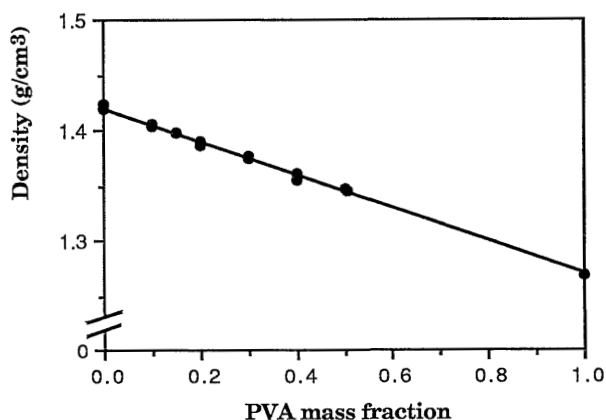
Figure 2. Density of the PAA–PVA blend at 22.5 °C, as a function of the blend composition: density of amorphous PVA = 1.27 g/cm³ [23].

3.2. Pervaporation characteristics of the PAA–PVA blend

The separation of alcohol-toluene mixtures through poly(acrylic acid)–poly(vinyl alcohol) blend membranes was evaluated to investigate the polymer blend concept in developing membrane materials. Since this study was focussed on the selective removal of alcohols from organic mixtures, poly(acrylic acid) (PAA) was selected as a polymer material based on its high affinity for alcohols. PAA is highly swollen or even soluble in the low molecular weight aliphatic alcohols like methanol and ethanol. In addition, PAA can preferentially interact with alcohols through hydrogen bond formation. To improve both mechanical stability and permselectivity towards alcohol-toluene liquid mixtures, PAA has been blended with poly(vinyl alcohol) (PVA) which is hardly swollen in alcohols. PVA is reported to be very selective for alcohols over hydrocarbons [24]. The pervaporation characteristics of the PAA–PVA blend membranes for the ethanol-toluene and the methanol-toluene liquid
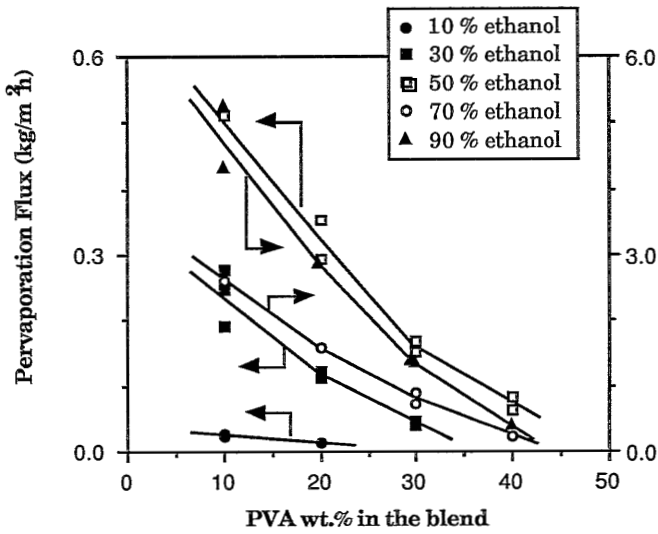
Figure 3a
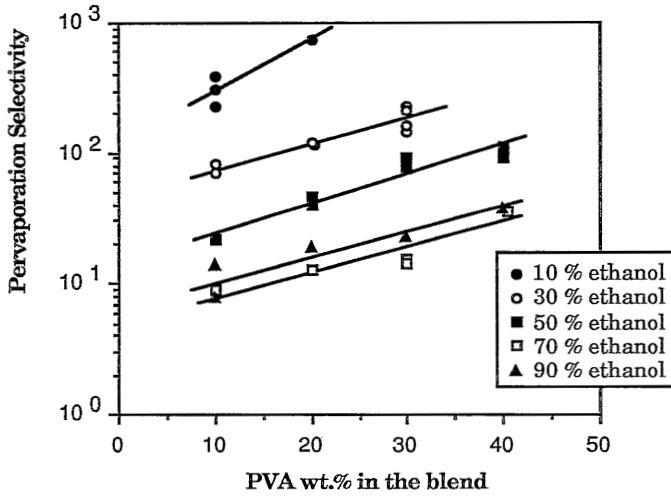
Figure 3b

Figure 3. Pervaporation characteristics of PAA–PVA blend membranes for ethanol-toluene liquid mixtures, as a function of the blend composition. (Note the different scale on the ordinates in figure 3a)
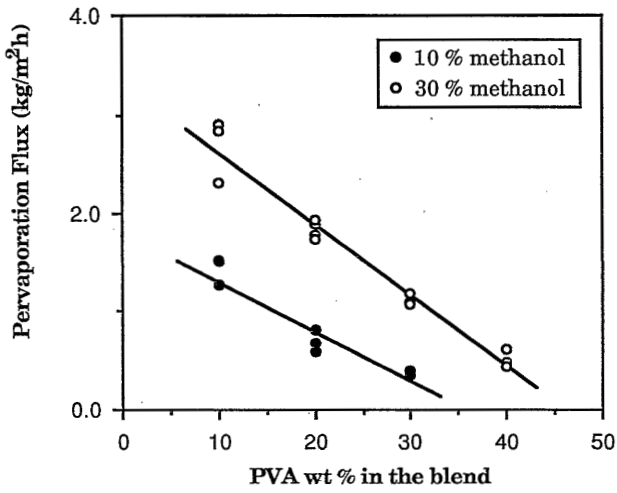
Figure 4a
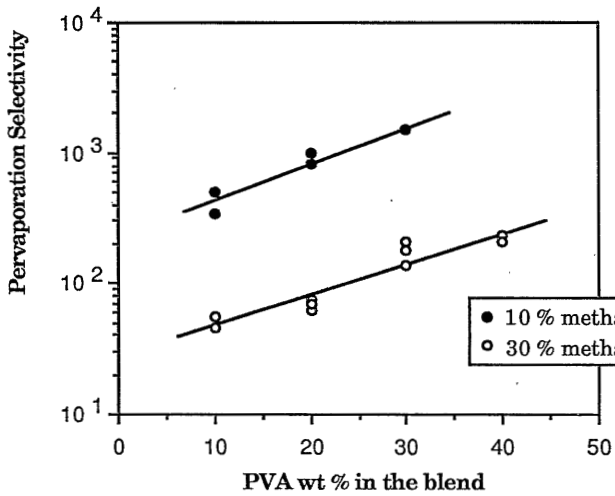
Figure 4b

Figure 4. Pervaporation characteristics of PAA–PVA blend membranes for methanol-toluene liquid mixtures, as a function of the blend composition.

mixtures are presented in figures 3 and 4, respectively. In these figures the flux and the selectivity are given as a function of the poly(vinyl alcohol) concentration in the blend. The fluxes of different membranes are normalized to a membrane thickness of 20 μm, and the selectivity is calculated according to equation (1). It can be observed, as expected, that the transport properties of the PAA–PVA blends depend strongly on the PAA/PVA ratio in the blend. The pervaporation flux decreases gradually for all feed mixtures with different compositions as the PVA content in the blends increases from 10 to 40 wt.%. These figures show that by controlling the PVA amount in the blend a great variety of fluxes can be obtained for any feed mixture. In the case of a feed mixture of ethanol-toluene (1/1 by wt), for example, a flux decline from 0.51 to 0.07 kg/m²h, about one order of magnitude, can be observed as the PVA content increases from 10 to 40 wt.%. The reason for this behavior is probably the reduced swelling of the blend membranes. Poly(acrylic acid) is soluble in ethanol, whilst poly(vinyl alcohol) is very little swollen in ethanol [25]. Therefore the higher the PVA content is, the less the membrane is swollen. This decreasing sorption ability results in a decreasing penetrant concentration in the membrane, and consequently results in a decreasing permeation rate.

The increasing content of poly(vinyl alcohol) in the membrane has a favorable effect on the selectivity. All membranes are selective to methanol and ethanol, and the selectivity increases with increasing PVA content in the blend.

The total flux J can be divided into the component flux of alcohol $J_{alcohol}$ and that of toluene $J_{toluene}$ by using the permeate composition data:

$$J_{alcohol} = J * y_{alcohol} \tag{2}$$
$$J_{toluene} = J * y_{toluene} \tag{3}$$

where $y_{alcohol}$ and $y_{toluene}$ are the concentrations of alcohol and toluene in the permeate, respectively. As an example, the component fluxes of a ethanol-toluene (1/1 by wt) mixture calculated from these equations are given in figure 5 as a function of the blend composition. This figure clearly indicates that for this system the increase in selectivity is attributed to a

more rapid decrease in the toluene component flux compared to ethanol with increasing PVA content. For all other mixtures the same trend is observed.
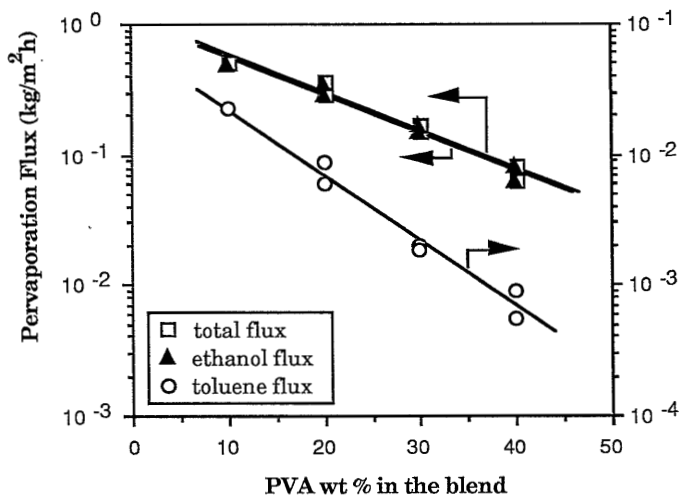

Figure 5. Total and component fluxes of an ethanol-toluene (1/1 by wt) mixture through PAA–PVA blend membranes, as a function of the blend composition.

3.3. Influence of the feed composition

The permeation of molecules through a nonporous polymer membrane is generally described by a solution-diffusion mechanism in a sequence of three steps; sorption, diffusion, and evaporation. According to this model the permselective properties of pervaporation membranes are determined by solubility and diffusivity of the permeating components in the membrane. Because generally both sorption and diffusion phenomena are dependent on the composition of the liquid mixture, also the permeation characteristics of membranes are usually strongly influenced by the feed composition.

The effect of the feed composition on the flux and selectivity was investigated over the whole mixture concentration range for ethanol-toluene mixtures. Figure 6 represents the effect of the feed composition on

the pervaporation fluxes. Although low fluxes are obtained when the ethanol content in the feed is low, the fluxes increase strongly for all blend membranes as the ethanol concentration increases. For instance, in the case of a blend membrane containing 10 wt.% poly(vinyl alcohol) the flux for the ethanol-toluene liquid mixture increases exponentially from 0.025 to 4.8 kg/m^{2}h, i.e. more than two orders of magnitude, as the ethanol concentration increases from 10 to 90 wt.%. For all the other blends the same trend is observed, which indicates a strong interaction between the membrane and the feed mixture components.

Figure 7 shows the ethanol concentration in the permeate as a function of the feed composition together with the vapor-liquid equilibrium curve of the ethanol-toluene mixtures at 30 °C for comparison. The vapor-liquid equilibrium data were calculated from the Wilson equation with parameters obtained from the literature [26]. For all blends tested the ethanol concentration in the permeate was higher than 95 wt.%. This is much higher than the ethanol concentration in the vapor which is in equilibrium with the liquid. Furthermore the separation problem of the azeotrope could easily be overcome.
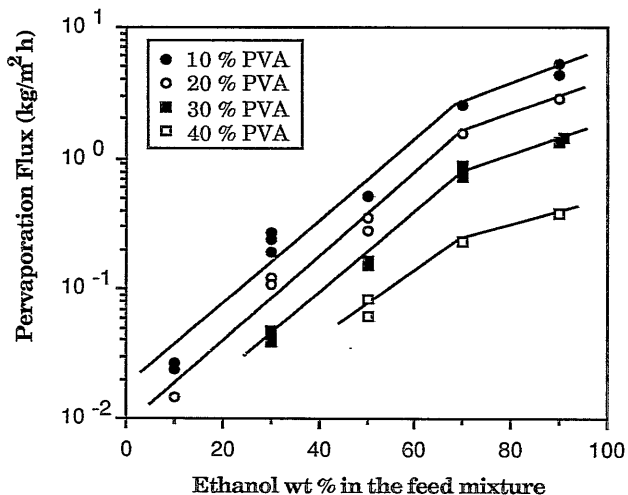
Figure 6. Influence of the feed composition on the pervaporation flux of ethanol-toluene mixtures through various PAA–PVA blend membranes.
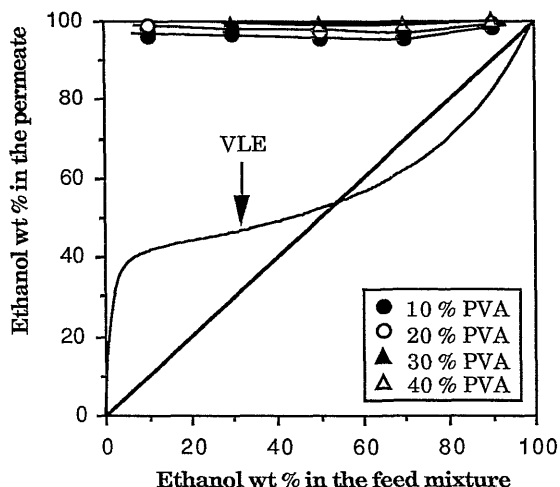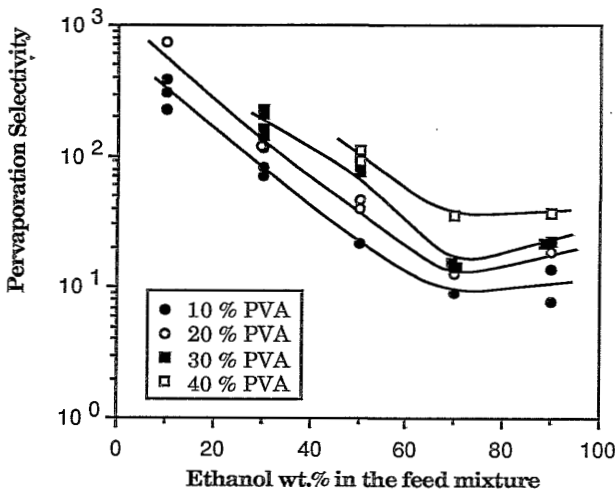
Figure 7. Permeate composition in the pervaporation of ethanol-toluene mixtures through various PAA–PVA blend membranes, as a function of the feed composition. The vapor-liquid equilibrium curve is also given.

The selectivity values are presented in figure 8. The selectivity first decreases with increasing ethanol content up to 70 wt.%, and then remains more or less constant. This seems to be related to the variation in the component flux of toluene. Figure 9 represents the component fluxes of ethanol and toluene for the ethanol-toluene liquid mixtures. It is clearly seen from this figure that the component flux of ethanol for the blends of various compositions follows practically the same trend and the same degree of variation as the total flux with increasing ethanol content in the feed mixture (compare figure 9a with figure 6). However the toluene flux shows a different dependency (see figure 9b). These fluxes first increase exponentially as the ethanol concentration increases up to 70 wt.%. However as the ethanol concentration increases from 70 to 90 wt.%, the toluene fluxes decrease. In the concentration range below 70 wt.% ethanol, the slope of the increase in the toluene fluxes is steeper compared to ethanol. This more rapid increase of the toluene fluxes causes a loss in selectivity. However in the ethanol concentration range between 70 and 90 wt.%, the ratio of component fluxes of ethanol and toluene is equal to the concentration ratio of ethanol and toluene in the feed mixture. Hence the

selectivity remains constant.

The initial increase in the toluene component fluxes might be related to the swelling of the membranes. When a penetrant i diffuses through a membrane, the flux J_i is the product of the concentration C_i and the linear velocity v_i of the penetrant inside the membrane. The velocity is the product of mobility B_i and driving force. In the case of pervaporation the driving force is a gradient in the chemical potential across the membrane, i.e., $- d\mu_i/dx$. Therefore the following relation expresses the flux in a pervaporation process:

$$J_i = v_i \, C_i = - C_i \, B_i \, d\mu_i/dx \tag{4}$$

According to this relation the flux should decrease as the activity, i.e. the chemical potential, of a mixture component in the feed decreases because the activity in the permeate side is kept constant by a continuous evacuation. However in the concentration range of ethanol 10 to 70 wt.% the toluene permeability increases despite the decreasing activity. A possible explanation for this contradicting phenomenon might be the

Figure 8. Influence of the feed composition on the pervaporation selectivity of ethanol-toluene mixtures through various PAA–PVA blend membranes.
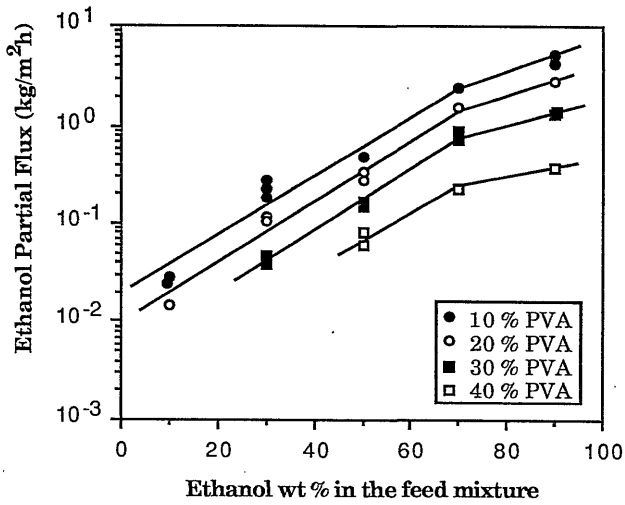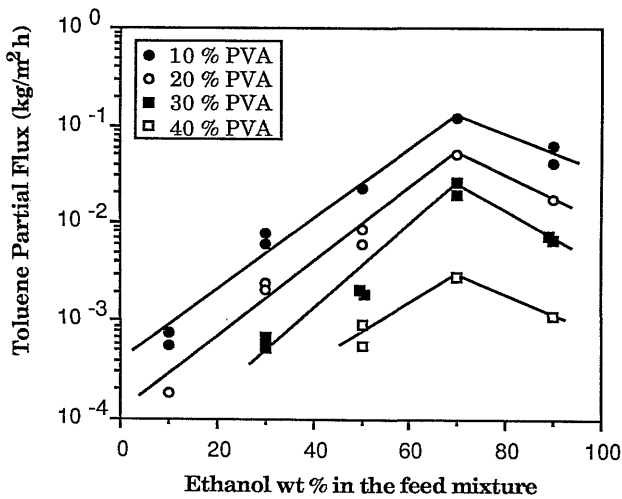
Figure 9a

Figure 9b

Figure 9. Component fluxes of ethanol (figure 9a) and toluene (figure 9b) through various PAA–PVA blend membranes as a function of the ethanol concentration in an ethanol-toluene liquid mixture.

plasticization of the polymer matrix by the sorbed ethanol molecules. As liquid molecules are more sorbed into a polymer, then the polymer matrix becomes looser. In chapter 4 of this thesis experimental evidence will be given from sorption measurements showing an increasing sorption of ethanol-toluene liquid mixtures with increasing ethanol content in the mixtures. In a more swollen membrane the toluene molecules can permeate faster. At the same time, however, the driving force for the toluene permeation is continuously decreasing. These two opposing terms are compensating each other. Until an ethanol concentration up to 70 wt.%, the effect of the plasticization of the polymer matrix seems to prevail over the decreasing driving force for the toluene permeation. Both effects should be of the same magnitude at around 70 wt.% ethanol in the feed. At higher ethanol concentrations the effect of the decreasing driving force might be predominant, which results in a decreasing toluene permeability.

3.4. Pervaporation of methanol-toluene mixtures

The pervaporation results for the methanol-toluene mixtures are given in figure 10. Here again the trend of the dependence of flux and selectivity on the feed composition is almost the same as that for the ethanol-toluene mixture. With increasing methanol concentration in the feed, the flux increases exponentially, while the selectivity first decreases and then remains constant.

From the comparison of the pervaporation characteristics of a methanol-toluene versus an ethanol-toluene mixture, it is observed that in the case of methanol-toluene the fluxes are much higher, about one order of magnitude, than in the case of ethanol-toluene for the same feed composition. This might be due to a different degree of interaction. Methanol shows a stronger affinity for the blend of poly(acrylic acid) and poly(vinyl alcohol) than ethanol since methanol is more polar and has a higher ability of hydrogen bonding. This stronger interaction results in a higher sorption, and thereby in a higher permeation rate of the methanol mixture than the ethanol mixture (the experimental evidence for the higher sorption of the methanol mixture is given in chapter 4 of this thesis). In addition, the difference in molecular size favors the permeability of methanol as well. The molar volume of methanol is about
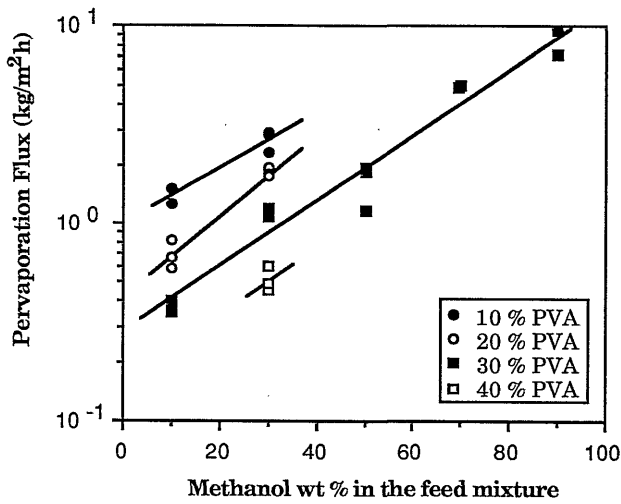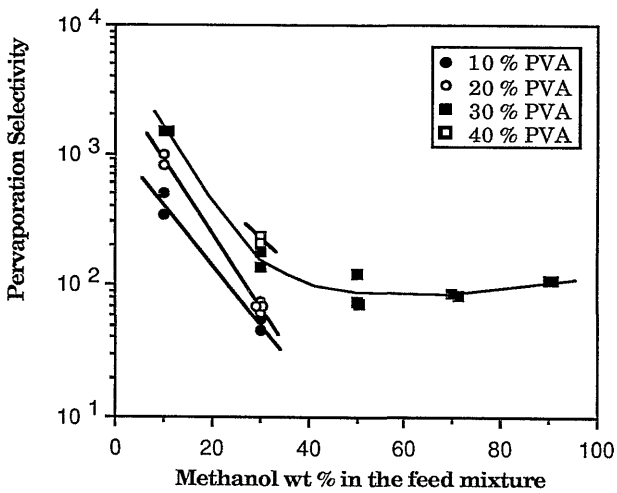
Figure 10a

Figure 10b

Figure 10. Pervaporation flux and selectivity of methanol-toluene liquid mixtures through various PAA–PVA blend membranes, as a function of the feed composition.

two thirds of that of ethanol, which implies that methanol, the smaller molecule, will permeate faster through a membrane than ethanol. Another reason is the difference in the activities of methanol and ethanol in a mixture with toluene. For example, the activity of methanol in a methanol-toluene mixture at 10 wt.% methanol is 0.76, while the ethanol activity in an ethanol-toluene mixture at the same concentration is 0.62. Such a difference in activity results in a difference in driving force, and consequently in a difference in the pervaporation flux.

Despite the higher flux with the methanol mixture, the selectivities for both mixtures at lower alcohol content are about equal. This may be explained in terms of coupling phenomena. The higher permeation of methanol seems to be compensated by a higher permeation of toluene with roughly the same factor.

4. CONCLUSIONS

Transparent homogeneous membranes could be prepared from a polymer blend of poly(acrylic acid) with poly(vinyl alcohol). Their pervaporation properties were investigated by using methanol-toluene and ethanol-toluene liquid mixtures. For both mixtures high fluxes and high selectivities were observed, which were strongly dependent on the blend composition. The flux decreased gradually as the PVA content in the blends increased, whereas the selectivity increased. It implies that such a polymer blend can offer a convenient way to optimize the separation characteristics of a membrane for a particular separation task. This means that the separation characteristics of a blend membrane can easily be adjusted by varying the blend composition.

It was also observed that the membrane performance was strongly influenced by the feed mixture composition. For both mixtures the flux increased exponentially, but the selectivity decreased with increasing alcohol concentration in the feed.

In the case of methanol-toluene mixtures the fluxes are much higher, about one order of magnitude, compared to ethanol-toluene mixtures for the same feed composition (% by weight). This is due to a stronger affinity of methanol for the PAA–PVA blends than ethanol. This stronger interaction results in a higher sorption, and thereby in a higher flux of the

methanol mixtures. In addition, the difference in the molecular size between methanol and ethanol favors the permeability of the smaller methanol as well.

REFERENCES

1. R.C. Binning, R.J. Lee, J.F. Jennings, and E.C. Martin, *Ind. Eng. Chem.*, 53(1) (1961) 45-50.

2. E.C. Martin, R.C. Binning, L.M. Adams, and R.J. Lee, U.S. Pat. 3,140,256 (1964).

3. J.W. Carter and B. Jagannadhaswamy, *Brit. Chem. Eng.*, 9(8) (1964) 523-526.

4. J.M. Stuckey, US Pat. 2,930,754 (1960); 2,958,656 (1960); and 3,043,891 (1962).

5. H.C. Park, "Separation of Nonaqueous Organic Liquid Mixtures by Pervaporation", Internal report, University of Twente, Enschede, The Netherlands (1989).

6. C. Herion, "Zum Verhalten Asymmetrischer Membranen in der Pervaporation", Ph.D. thesis, Rheinisch - Westfälischen Technischen Hochschule Aachen, Aachen, Germany (1988). pp. 150-165

7. K. Ishihara, K. Matsui, H. Fujii, H. Nishide, and I. Shinohara, *Chem. Letters*, (1985) 1663-1666.

8. F. Suzuki, K. Onozato, H. Yaegashi, and T. Masuko, *J. Appl. Polym. Sci.*, 34 (1987) 2197-2204.

9. G. Chen, F. Lu, B. Wu, Y. Shi, S. Zhang, and C. Zhang, "Pervaporation of Organic Liquid Mixtures through Polyphenylquinoxaline Membranes", Proc. of 3rd Int'l. Conf. on Pervapor. Processes in the Chem. Ind., Nancy, France, Sept. 1988. pp. 188-193

10. H. Ohst, K. Hildenbrand, and R. Dhein, "Polymer Structure/Properties – Correlation of Polyurethane PV-Membranes for Aromatic/Aliphatic Separation", Proc. of 5th Int'l. Conf. on Pervapor. Processes in the Chem. Ind., Heidelberg, Germany, March 1991. pp. 7-21

11. P. Aptel, J. Cuny, J. Jozefonwicz, G. Morel, and J. Néel, *J. Appl. Polym. Sci.*, 18 (1974) 351-364.

12. P. Aptel, J. Cuny, J. Jozefowicz, G. Morel, and J. Néel, *J. Appl. Polym. Sci.*, 16 (1972) 1061-1076.

13. G. Ellinghorst, A. Niemöller, H. Scholz, M. Scholz, and H. Steinhauser, "Membranes for Pervaporation by Radiation Grafting and Curing and by Plasma", Proc. of 2nd Int'l. Conf. on Pervapor. Processes in the Chem. Ind., San Antonio, Texas, March 1987. pp. 79-99

14. E.C. Martin and J.T. Kelly, US Pat. 2,981,730 (1961).

15. E.C. Martin, R.C. Binning, L.M. Adams, and R.J. Lee, U.S. Pat. 3,140,256 (1964).

16. S. Yamada and T. Hamaya, *J. Memb. Sci.*, 17 (1984) 125-138.

17. I. Cabasso, J. Jagur-Grodzinski, and D. Vofsi, *J. Appl. Polym. Sci.*, (1974) 2117-2136 and 2137-2147.

18. I. Cabasso, *Ind. Eng. Chem. Prod. Res. Dev.*, 22 (1983) 313-319.

19. Q.T. Nguyen, "Polymer Blending Concept for the Preparation of Permselective Membranes (For Pervaporation)" in: *Synthetic Polymeric Membranes*, ed. by B. Sedlacek and J. Kahovec, Walter de Gruyter & Co., Berlin (1987). pp. 479-494

20. Z. Yun, M.-Y. Huang, and Y.-Y. Jiang, Polym. Bulletin, 20 (1988) 277-284.

21. E. Ruckenstein and J.S. Park, *J. Appl. Polym. Sci.*, 40 (1990) 213-220.

22. F.E. Karasz, Ch. 2 in: *Polymer Blends and Mixtures*, ed. by D.J. Walsh, J.S. Higgins, and A. Maconnachie, NATO ASI Series, Martinus Nijhoff, Dordrecht (1985).

23. R.L. Miller, "Crystallographic Data for Various Polymers" in: *Polymer Handbook*, 3rd ed., ed. by J. Brandrup and E.M. Immergut, John Wiley & Sons, New York (1989). pp. VI/1-VI/208

24. W.H. Schneider, "Purification of Anhydrous Organic Mixtures by Pervaporation", Proc. of 2nd Int'l. Conf. on Pervapor. Processes in Chem. Ind., San Antonio, Texas, March 1987. pp. 169-175

25. J.W.F. Spitzen, E. Elsinghorst, M.H.V. Mulder, and C.A. Smolders, "Solution-Diffusion Aspects in The Separation of Ethanol/Water Mixtures with PVA Membranes", ibid. pp. 209-224

26. J. Gmehling, U. Onken, and J.R. Rarey-Nies, *Vapor-Liquid Equilibrium Data Collection: Chemistry Data Series; Vol. 1, Part 2e*, DECHEMA, Frankfurt/Main, Germany (1988). p. 370

Chapter *4*

SORPTION OF ALCOHOL–TOLUENE MIXTURES IN PAA–PVA BLEND MEMBRANES AND ITS ROLE ON PERVAPORATION

Summary

In order to obtain more information on the separation mechanism in pervaporation, equilibrium sorption experiments were carried out. The overall and preferential sorption of alcohol-toluene mixtures in homogeneous blends of poly(acrylic acid) and poly(vinyl alcohol) were determined to investigate the influence of blend composition and of liquid mixture composition. Both the overall solubility and the equilibrium sorption selectivity were strongly dependent on the composition of the blend and of the liquid feed mixture. The swelling of the blends increased with increasing poly(acrylic acid) content, and with increasing alcohol content in the liquid mixtures. Alcohols were sorbed preferentially over toluene in all cases tested. The equilibrium sorption selectivity increased with increasing poly(vinyl alcohol) content in the blends, and with decreasing alcohol content in the liquid mixtures.

The equilibrium sorption selectivity was predicted by a model which was derived from Flory-Huggins thermodynamics. The agreement between the predicted and the experimental results was very good.

In addition the equilibrium sorption results were compared with the pervaporation results to evaluate the influence of sorption and diffusion on the overall pervaporation process. It can be concluded from this comparison that preferential sorption dominates the pervaporation selectivity in the systems studied.

1. INTRODUCTION

The unique feature of pervaporation is the mass transfer from a liquid phase to a vapor phase through a non-porous polymeric membrane. When a liquid mixture is brought into contact with a membrane at one side, it is sorbed into the membrane. Due to a driving force applied across the membrane, the sorbed liquid molecules permeate through the membrane and evaporate at the downstream side of the membrane. This three step mechanism of transport can be described by a solution-diffusion model, and it is generally accepted for describing the mass transfer in pervaporation. In this model the diffusion step is assumed to be slow compared to the other two steps, and consequently the rate-determining step. The swelling state of the membrane at both interfaces is assumed to be equivalent with the thermodynamic equilibrium swelling of the membrane being in contact with the feed liquid and the downstream vapor phase, respectively. In pervaporation the permeated species are usually removed from the downstream side under a relatively low vapor pressure, for example by evacuation with a vacuum pump. As far as this condition is fulfilled, the evaporation step can be considered to be much faster than sorption or diffusion. Hence evaporation does not contribute to permselectivity. Therefore the separation by pervaporation results from the differences in the preferential sorption of the individual components of a mixture into the membrane together with the diffusion rates through the membrane. This postulation implies that both sorption and diffusion phenomena have to be accounted for to understand the physico-chemical nature of the pervaporation separation process.

It is impossible to investigate experimentally sorption and diffusion processes separately because they take place simultaneously. Based on the above consideration, however, the results of thermodynamic equilibrium sorption experiments can be used to obtain information on the sorption process during pervaporation. The sorption of a binary liquid mixture in a polymer is characterized by two parameters; (i) overall sorption and (ii) preferential sorption. The overall sorption represents the total amount of liquid inside the polymer. The preferential sorption is a measure for the difference of the liquid compositions in the binary liquid phase compared to that in the polymer phase.

When a polymer is in contact with a binary liquid mixture, normally one of the mixture components is preferentially sorbed into the polymer.

This preferential sorption phenomenon is of special interest in the pervaporation process. Many authors have assumed an ideal additive behavior for component solubilities [1-4]. In this case, the amount of each component sorbed in the polymeric membrane Q_i^m is assumed to be proportional to its activity a_i in the liquid mixture and the single liquid solubility Q_i° in the membrane: $Q_i^m = a_i Q_i^\circ$. This equation implies that ideal preferential sorption occurs, which can be derived from pure component sorption data. However deviations from an ideal sorption are usually observed experimentally for the sorption of various liquid mixtures in polymers [5-9]. Furthermore it is quite often observed that the component that is sorbed preferentially also permeates preferentially. In other words, preferential sorption is the leading factor in selective transport. A good overview of literature sources which confirm this observation has been given by Mulder [10].

In this study equilibrium sorption experiments were carried out in order to obtain more information on the separation mechanism. The overall and preferential sorption characteristics of alcohol-toluene liquid mixtures in the poly(acrylic acid) and poly(vinyl alcohol) blend membranes were studied as a function of the blend composition and the binary liquid mixture composition as well. In addition the equilibrium sorption results were compared with the pervaporation results to evaluate the influence of sorption on the overall pervaporation process.

2. EXPERIMENTAL

2.1. Materials

Poly(acrylic acid) (PAA) (Mw = 250,000 g/mol) and poly(vinyl alcohol) (PVA) (96% hydrolyzed, Mw = 85,000 ~ 146,000 g/mol) were supplied by Aldrich Chemical Co. Methyl alcohol, ethyl alcohol and toluene (analytical grade) were purchased from Merck Co. They were used without any further purification. Water was demineralized before use.

2.2. Preparation of polymer films

Poly(acrylic acid) and poly(vinyl alcohol) were separately dissolved in water. The two solutions were mixed together in various proportions to obtain the proper casting solutions. Homogeneous polymer films were prepared by casting the polymer solution on a Perspex plate with a casting knife. The solvent, water, was slowly removed by evaporation under a flowing nitrogen stream at room temperature. The thickness of the resulting polymer films was about 100 μm.

2.3. Sorption experiments

Strips of polymer films were first dried for 2~4 days in a flowing nitrogen atmosphere and then for 2 days in a vacuum oven at room temperature. The dried sample strip (about 1 g) was immersed in a closed bottle containing either methanol, ethanol, toluene, or a mixture of these solvents. The bottle was placed in a thermostated bath at 30 °C. After the swelling equilibrium state was reached, the strip was removed from the bottle and put into a closed tube after the surface liquid was quickly removed with tissue papers. The sorbed liquid was distilled out of the sample by a laboratory vacuum apparatus described by Mulder et. al [8]. The composition of the distilled sorbate was analyzed by gas chromatography equipped with a thermal conductivity detector.

The overall solubility Q is calculated from the weight of the swollen and the dry polymer sample, and is expressed in units of grams of sorbed liquid per 1 gram of dry polymer. The sorption selectivity α_S is determined from the composition of the distilled liquid, and defined in the same way as the pervaporation selectivity:

$$\alpha_S = (y_1/y_2) / (x_1/x_2) \tag{1}$$

where x and y represent the concentrations in the binary liquid mixture and in the sorbed liquid, respectively. Index 1 refers to the preferentially soluble component, methanol or ethanol in this study, and index 2 refers to toluene.

3. RESULTS AND DISCUSSION

3.1. Single liquid sorption

The sorption results for pure methanol and ethanol in the blend membranes of poly(acrylic acid) and poly(vinyl alcohol) are given in figure 1. From this figure it can be observed that the solubilities of both methanol and ethanol decrease strongly with increasing PVA content in the blend. This can be related to the affinity of the PAA–PVA blend towards these alcohols which decreases with increasing PVA content.

The affinity between a polymer and a solvent can be expressed in terms of an interaction parameter. In the case of equilibrium sorption of a pure solvent in a polymer, the binary interaction parameter χ_{ip} can be calculated from the following equation, which is derived from the Flory-Rehner theory [11] by omitting the elastic free energy contribution:

$$\Delta\mu_i/RT = \ln(1 - \phi_p) + \phi_p + \chi_{ip}\,\phi_p{}^2 = 0 \tag{2}$$

Here, ϕ_p is the volume fraction of the polymer, and can be determined from an equilibrium sorption experiment.

The calculated interaction parameters are given in figure 2. This figure shows that the binary interaction parameters between methanol and the blend and between ethanol and the blend increase as the PVA content in the blend increases. This means that the affinity of the blends towards both alcohols decreases. In addition, methanol shows lower interaction parameter values, so a better affinity, than ethanol over the whole blend composition tested.

The decreasing affinity of the blends towards methanol and ethanol with increasing PVA content can be explained in terms of the difference in affinity of the individual polymers for these alcohols. PAA is soluble in methanol and ethanol, while PVA shows a very low solubility for these alcohols [9,12]. For instance, the ethanol sorption value in PVA is about 0.08 g/g dry polymer. Since generally the properties of a two-component homogeneous blend is in between those of the two component polymers being related to the composition of the blend, the overall affinity of the PAA–PVA blend for the alcohols should decrease with increasing PVA content in the blend. This was confirmed from the measurements of single liquid solubilities of methanol and ethanol: a decreasing affinity

resulted in a decreasing solubility.

Contrary to the high alcohol solubility, all the tested blends showed hardly any sorption for toluene. The absolute value of toluene solubility was found to be less than 0.001 g/g dry polymer, which is in the range of the experimental error.
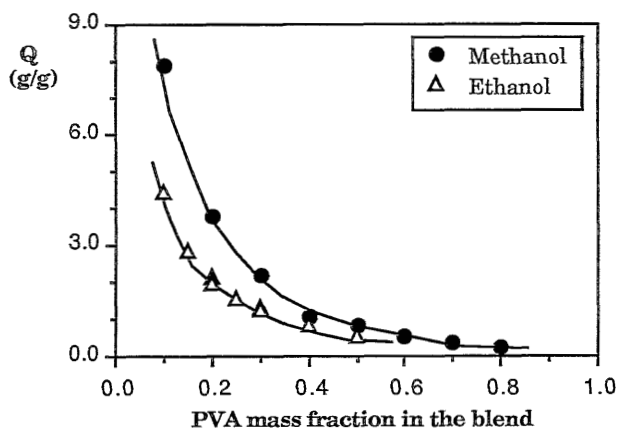

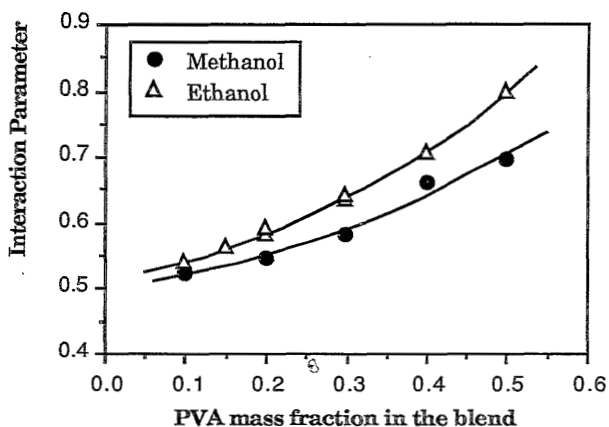*Figure 1. Pure solvent solubility Q of methanol and ethanol in PAA–PVA blends at 30 °C.*

Figure 2. Interaction parameters of PAA–PVA blends at varying compositions with methanol and ethanol at 30 °C.

3.2. Influence of the blend composition

The influence of the blend composition on the overall and preferential sorption was investigated over the blend composition range of PVA 10 to 40 wt.%. The results for ethanol-toluene liquid mixtures are presented in figures 3 and 4.

In figure 3 the overall solubility Q is given as a function of the blend composition. This figure shows that as the PVA content in the blend increases, the overall solubility decreases exponentially. Since the PAA–PVA blend is hardly swollen in toluene, the overall solubility behavior of the ethanol-toluene liquid mixture is to a large extent governed by the solubility characteristics of ethanol. Therefore the decreasing overall solubility can be explained on the basis of the affinity of individual polymers for these alcoholic mixtures in a similar way as the sorption of pure ethanol.

The sorption selectivity increases gradually with increasing PVA content in the blends for all liquid mixtures with different compositions (figure 4). This is due to a rapid decrease of the component solubility of toluene. Component solubilities of both ethanol and toluene are given in figures 5 and 6, respectively. These figures clearly show that with increasing PVA content the component solubility of toluene decreases more rapidly than that of ethanol. For instance, in the sorption of an ethanol-toluene (1/1 by wt) mixture a decrease from 1.42 to 0.37 g/g dry polymer is observed for ethanol, but from 0.11 to 0.005 g/g dry polymer for toluene with increasing PVA content from 10 to 40 %.

3.3. Influence of the liquid mixture composition

The influence of the liquid mixture composition on the sorption characteristics was investigated for methanol-toluene and ethanol-toluene liquid mixtures over the whole mixture composition range.

In figures 7 and 8 the overall solubilities of these liquid mixtures in various poly(acrylic acid)–poly(vinyl alcohol) blends are given as a function of the liquid mixture composition, respectively. These figures show that all the tested blends have a parallel swelling behavior for the methanol and the ethanol mixtures. The overall solubilities of both liquid mixtures increase exponentially with increasing alcohol content. This
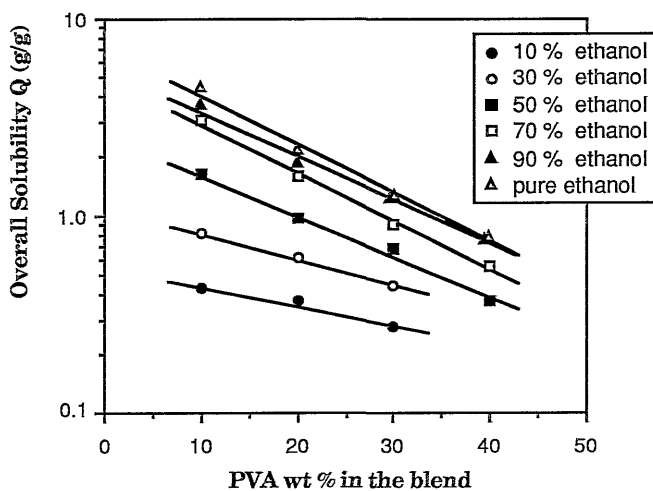
Figure 3. Effect of the blend composition on the overall solubility Q of ethanol-toluene liquid mixtures in PAA–PVA blend membranes.
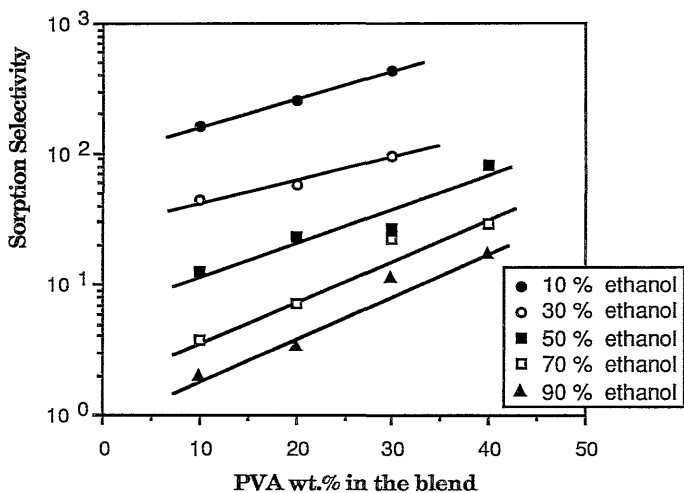

Figure 4. Effect of the blend composition on the sorption selectivity of ethanol-toluene liquid mixtures in PAA–PVA blend membranes.
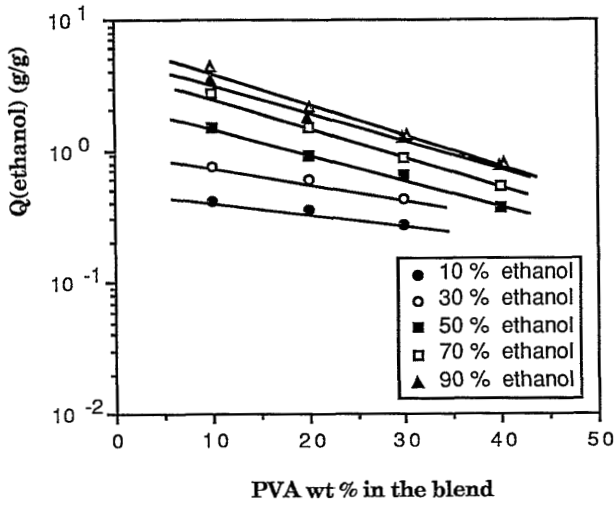
Figure 5. The component solubility of ethanol $Q_{(ethanol)}$ in PAA–PVA blend membranes, as a function of the blend composition.
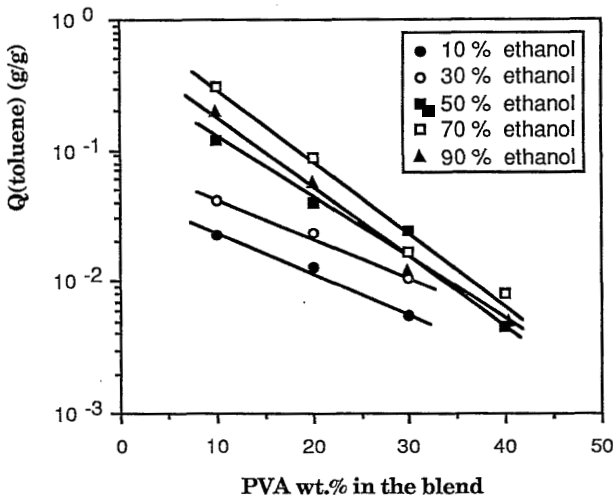

Figure 6. The component solubility of toluene $Q_{(toluene)}$ in PAA–PVA blend membranes, as a function of the blend composition.

can be explained by the much better affinity of these alcohols towards the PAA–PVA blend compared to toluene. As the alcohol content in the liquid mixtures increases, the affinity of the liquid mixtures towards the blend increases, and as a consequence the overall solubilities increase. In addition, the mass uptake of the methanol mixtures is about twice of that of the ethanol mixtures over the whole mixture composition range. This indicates that the methanol mixtures have a higher affinity.

The influence of liquid mixture composition on the preferential sorption of both liquid mixtures is presented in figures 9 and 10. From figures 9a and 10a it can be seen that both alcohols are preferentially sorbed over the whole feed composition range with alcohol concentrations of more than 80 wt.% in the sorbed liquids. The equilibrium sorption selectivity values are given in figures 9b and 10b. All tested blends show high sorption selectivities for the liquid mixtures containing small amounts of alcohol. However the sorption selectivity decreases drastically with increasing alcohol content in the liquid mixtures. At alcohol concentrations higher than 50 wt.%, the sorption selectivity values of both liquid mixtures are almost equal. However, for the alcohol-lean feed compositions the methanol mixtures show a much higher selectivity than the ethanol mixtures. The selectivity values for the methanol mixture at 10 wt.% methanol range from 400 to 2000, while in the case of the ethanol mixture values of 200 to 500 are obtained for the same composition.

3.4. Prediction of the preferential sorption

The preferential sorption of a binary liquid mixture into a polymer membrane can be described by the following expression which has been derived from Flory-Huggins thermodynamics by Mulder et al. [8]:

$$\ln\left(\frac{\phi_1}{\phi_2}\right) - \ln\left(\frac{v_1}{v_2}\right) = (l-1)\ln\left(\frac{\phi_2}{v_2}\right) - g_{12}(v_2)(v_1 - v_2) + g_{12}(u_2)(\phi_1 - \phi_2)$$

$$-\phi_3(\chi_{13} - l\chi_{23}) + u_1\phi_2\frac{\partial g_{12}}{\partial u_2} - v_1 v_2 \frac{\partial g_{12}}{\partial v_2} \tag{3}$$

The indices 1 and 2 refer to the binary liquid components (taking 1 for the preferentially soluble liquid), and the index 3 to the polymer membrane.
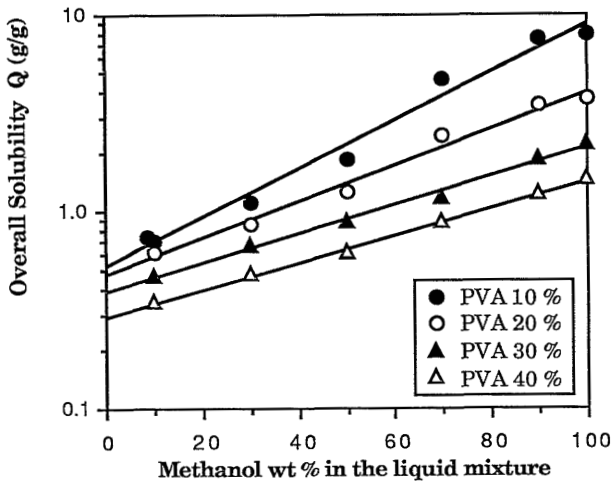
Figure 7. Overall solubility Q of methanol-toluene liquid mixtures in PAA–PVA blend membranes as a function of liquid mixture composition.
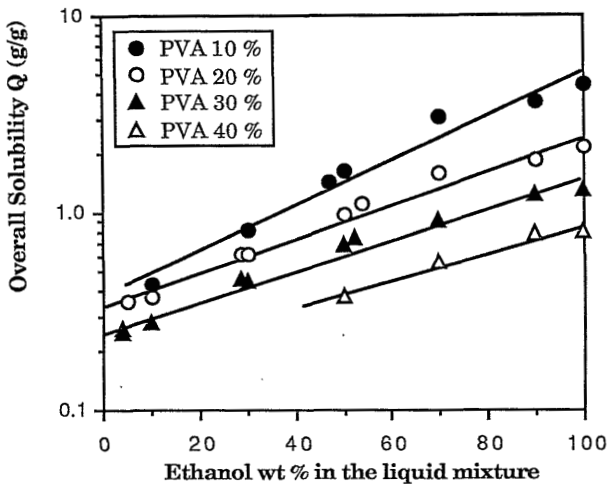

Figure 8. Overall solubility Q of ethanol-toluene liquid mixtures in PAA–PVA blend membranes as a function of liquid mixture composition.
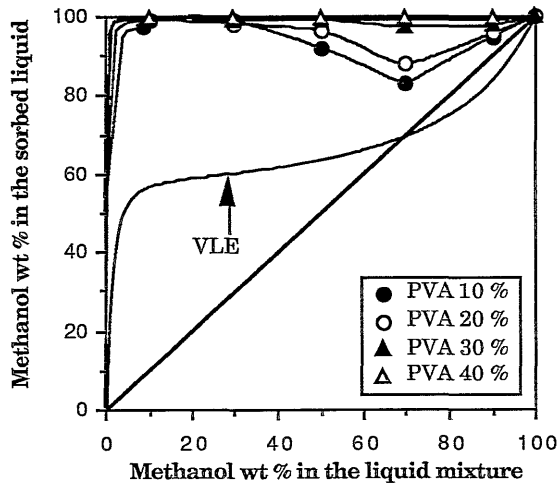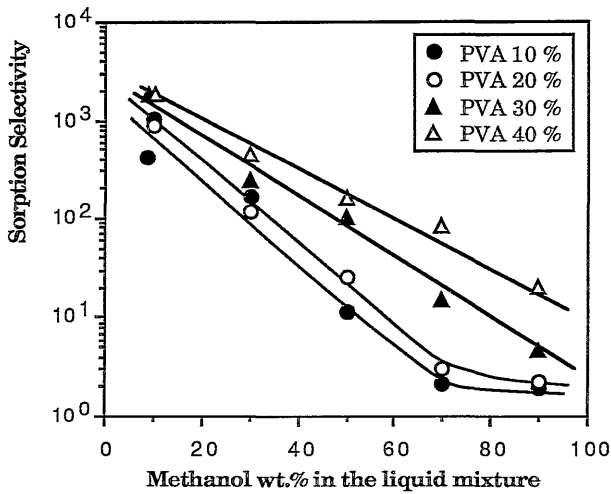
figure 9a

figure 9b

Figure 9. Composition of the sorbed liquid (a) and sorption selectivity (b) of methanol-toluene liquid mixtures in PAA–PVA blend membranes as a function of liquid mixture composition.

figure 10a

figure 10b

Figure 10. Composition of the sorbed liquid (a) and sorption selectivity (b) of ethanol-toluene liquid mixtures in PAA–PVA blend membranes as a function of liquid mixture composition.
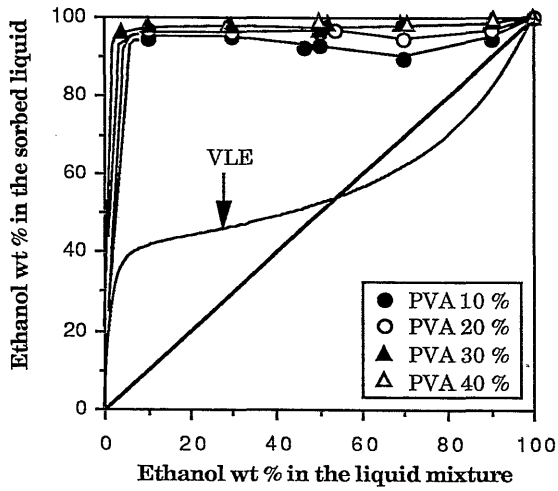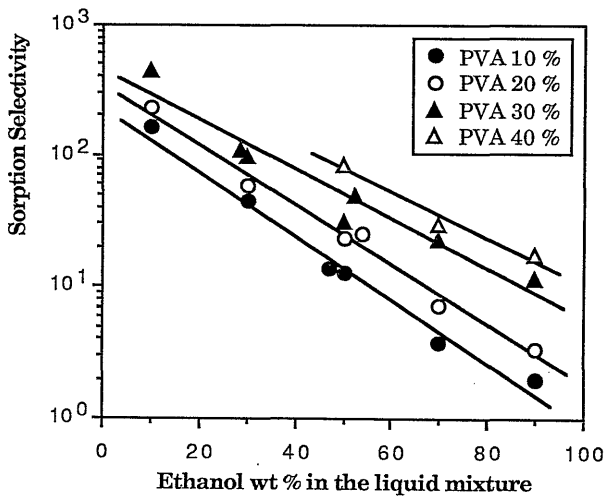
v_i represents the volume fraction of the liquid i in the binary liquid mixture. The volume fraction of the component i in the ternary polymeric phase is denoted by ϕ_i with $\phi_1 + \phi_2 + \phi_3 = 1$. The volume fraction of the liquid i of the liquid mixture in the polymeric phase is denoted by $u_i = \phi_i / (\phi_1 + \phi_2)$. l is the ratio of molar volumes of liquids 1 and 2. This equation is very useful for understanding the influence of governing factors for the preferential sorption, as discussed in the appendix.

Equation (3) was used to predict the preferential sorption of ethanol-toluene mixtures in PAA–PVA blend membranes. In this case the indices 1 and 2 refer to ethanol and toluene, respectively. Their physical properties are given in table 1. The binary interaction parameter g_{12} between ethanol and toluene at 30 °C was calculated from the Wilson equation using vapor-liquid equilibrium data taken from the literature [13]. The dependency of g_{12} on the volume fraction of toluene was fitted to a fourth grade polynomial relation:

$$g_{12}(x) = 1.059 - 0.997\,x + 9.298\,x^2 - 17.688\,x^3 + 11.459\,x^4 \tag{4}$$

This relation was used not only for the liquid feed, but also for the sorbed liquid under the assumption that g_{12} is only dependent on the liquid composition.

The binary interaction parameters between the liquid components and the polymer, χ_{13} and χ_{23}, were assumed to be concentration independent and were calculated from the single liquid sorption data using equation (2). The sorption values of pure ethanol in the blend membranes and the calculated χ_{13} values are given in table 2. In this calculation the linear additivity of partial molar volumes was assumed.

Table 1. Physical properties of ethanol and toluene.

Liquid	Mw (g/mol)	molar volume (cm^3/mol, 25 °C)	molar volume ratio ethanol/toluene
Ethanol	46.07	58.69	0.5493
Toluene	92.15	106.85	—

Unfortunately it was impossible to obtain very precise data of the pure toluene sorption into the blend membranes because they were extremely low; less than 0.1 g/100 g dry membrane for all tested blends. Therefore the values of pure toluene sorption were assumed as 0.1 and 0.01 g/100 g dry membrane in order to obtain χ_{23} values. The calculated χ_{23} values are given in table 2.

To predict the preferential sorption by equation (3) one composition value should be known. For practical reasons ϕ_3 is used, since this parameter is obtained from overall sorption measurements.

The predicted and the experimentally determined preferential sorption results are presented in figure 11 for the blend membranes containing 10 to 40 wt.% PVA. Here the ethanol fraction in the sorbed liquid $C_1^{\,m}$ is plotted as a function of the ethanol fraction in the feed mixture $C_1^{\,f}$. When the pure toluene solubility was assumed to be 0.1 g/100 g dry polymer, the predicted ethanol concentrations inside the membranes were lower than the experimentally measured ones in all cases tested. However the liquid compositions in the membranes could be quantitatively predicted using a pure toluene solubility of 0.01 g/100 g dry polymer.

Table 2. The solubilities of pure ethanol and toluene in PAA–PVA blend membranes and the calculated interaction parameter values.

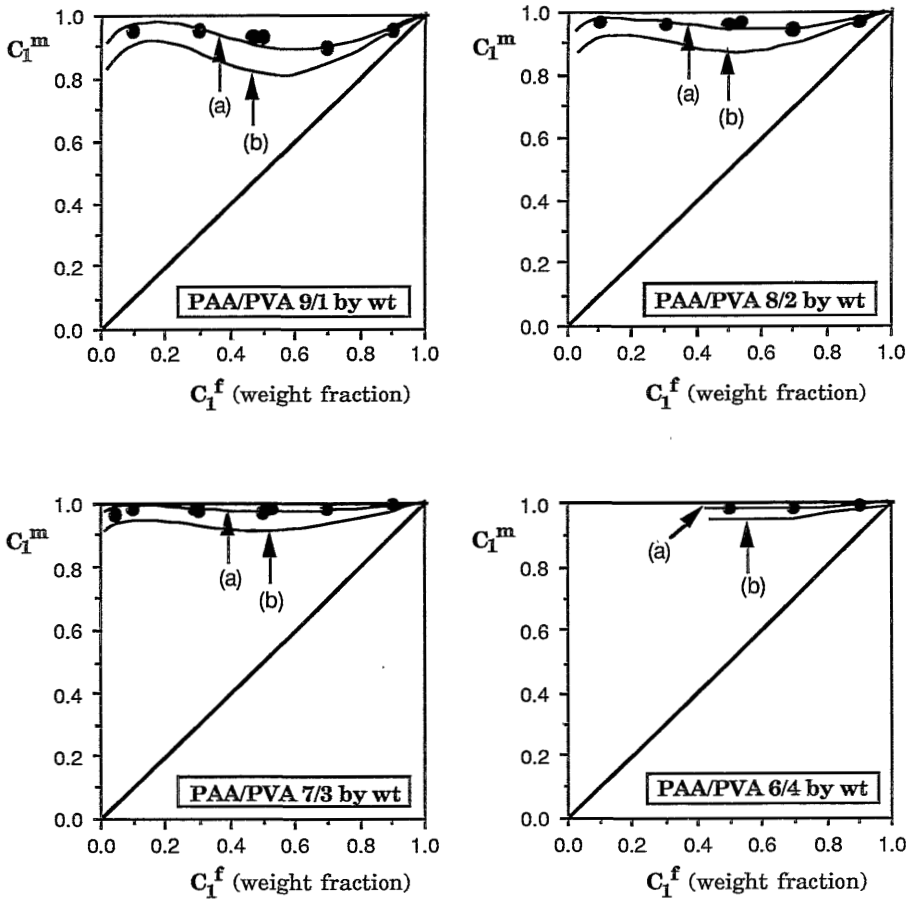| PVA content in the blend (wt.%)	density of the blend (g/cm^3)	ethanol solubility (g/100 g)	χ_{13}	toluene solubility* (g/100 g)	χ_{23}
10	1.404	442	0.541	0.01	7.73
				0.1	5.44
20	1.388	214	0.583	0.01	7.74
				0.1	5.45
30	1.376	128	0.634	0.01	7.75
				0.1	5.46
40	1.358	80.3	0.706	0.01	7.76
				0.1	5.47

* assumed values

Figure 11. Ethanol concentrations in the sorbed liquid C_1^m as a function of the ethanol content in ethanol/toluene feed mixtures C_1^f for various PAA–PVA blend membranes: ($\bullet$) experimentally measured, and (—) predicted with assumed pure toluene solubilities of 0.01 g (curve a) and 0.1 g/100 g dry polymer (curve b).

3.5. Sorption versus pervaporation

When a penetrant i diffuses through a membrane, the flux J_i is the product of the concentration C_i and the linear velocity k_i of the penetrant inside the membrane. The velocity is the product of mobility B_i and driving force. In the case of pervaporation the driving force is a gradient in the

chemical potential across the membrane, i.e., $-d\mu_i/dx$. Therefore the following relation expresses the flux in a pervaporation process:

$$J_i = k_i\, C_i = -\, C_i\, B_i\, d\mu_i/dx \tag{5}$$

Taking ideal conditions and an empirical exponential relationship for the concentration dependence of the diffusion coefficient, equation (5) can be transformed into a Fickian equation [10];

$$J_i = -\, D_i(C_i)\, dC_i/dx = -\, D_0\, \exp(\gamma\, C_i)\, dC_i/dx \tag{6a}$$

Here, D_0 is the diffusion coefficient at zero concentration, and γ is an exponential constant.

In a vacuum pervaporation the penetrant concentration at the downstream side membrane interface can be considered to be zero. Integration of equation (6a) with boundary conditions ($C_i = C_i^\circ$ at x = 0 and $C_i = 0$ at x = L) gives;

$$J = (D_0/\gamma L)\, [\exp(\gamma\, C_i^\circ) - 1] \tag{6b}$$

Here, L is the thickness of the membrane. From equation (6b) it can be seen that the permeation rate of a penetrant is a function of the penetrant concentration in the membrane, and increases with increasing penetrant concentration. In other words, the permeation rate of a penetrant is strongly dependent on the sorption ability of the penetrant into a polymer membrane.

In figure 12, the pervaporation fluxes are plotted versus the overall sorption values for methanol-toluene and ethanol-toluene mixtures. This figure includes all the experimental results obtained from poly(acrylic acid)–poly(vinyl alcohol) blend membranes containing 10 to 40 wt.% PVA. Although the spreading around the curves is substantial, a relation between flux and overall solubility can be observed for both liquid mixtures. The pervaporation flux increases exponentially with the concentration of penetrants in the membrane. This may indicate a general observation in the pervaporation process that diffusivity is an exponential function of penetrant concentration in a membrane [10]. In addition, a higher permeation rate of the methanol mixtures compared to the ethanol mixtures is observed over the whole penetrant concentration

range. This might be caused by the difference in molecular size between methanol and ethanol. The flux and solubility of these alcoholic mixtures are to a large extent governed by the properties of the corresponding alcohols since the permeate and the sorbed liquid consist mainly of methanol or ethanol. Therefore the methanol mixture can permeate faster since the molar volume of methanol is about two thirds compared to ethanol. It should be kept in mind that the penetrant concentration in the membrane is obtained from the equilibrium sorption experiments, whereas permeation is a non-equilibrium process. It is assumed that the sorption process is fast compared to the diffusion process implying that the concentration at the feed side of the membrane interface during permeation is equal to the equilibrium concentration. This may not always be the case. Some examples are known where the penetrant concentration in the membrane at the feed side during pervaporation is lower than the equilibrium sorption value [14-16].
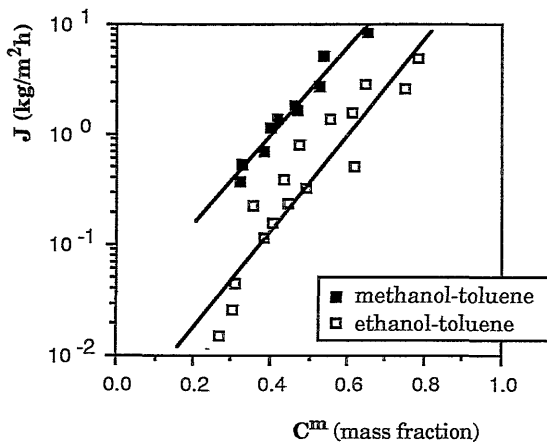

Figure 12. The relation between the pervaporation flux J and the overall equilibrium concentration C^m of the sorbed liquids in PAA–PVA blend membranes.

According to the solution-diffusion model the pervaporation selectivity is determined by the differences in solubility and diffusivity of penetrants in a membrane. Therefore by comparing the pervaporation selectivity α_p

and the sorption selectivity α_S the influence of diffusion can be deduced in terms of a diffusion selectivity α_D defined by [7,12]:

$$\alpha_D = \alpha_P / \alpha_S \qquad\qquad (7)$$

The diffusion selectivity value calculated in this way can give only qualitative information of the diffusion contribution to the separation in pervaporation.

Tables 3 and 4 summarize the three different selectivities for methanol-toluene and ethanol-toluene mixtures, respectively, for the blend membranes containing poly(vinyl alcohol) 10 to 40 wt.%. The diffusion selectivity values calculated from equation (7) are very small and can be neglected compared to pervaporation and sorption selectivity values at least for the low alcohol feed compositions. From this comparison it can be concluded that the separation of alcohol-toluene mixtures by pervaporation is dominated by the preferential sorption, and diffusion is only of minor importance in this separation process.

Table 3. Comparison of pervaporation, sorption, and diffusion selectivities for methanol-toluene liquid mixtures in PAA–PVA blend membranes.

PVA wt.% in the blend	selectivity (α)	methanol wt.% in the feed mixture				
		10 %	30 %	50 %	70 %	90 %
10	α_P	400	51			
	α_S	1038	169	11	2	2
	α_D	0.4	0.3			
20	α_P	900	69			
	α_S	873	119	25	3	2
	α_D	1.0	0.6			
30	α_P	1443	164	83	89	85
	α_S	1791	233	102	15	5
	α_D	0.8	0.7	0.8	5.9	17.0

Table 4. Comparison of pervaporation, sorption, and diffusion selectivities for ethanol-toluene liquid mixtures in PAA–PVA blend membranes.

PVA wt.% in the blend	selectivity (α)	ethanol wt.% in the feed mixture				
		10 %	30 %	50 %	70 %	90 %
10	α_P	344	73	22	9	10
	α_S	163	44	13	4	2
	α_D	2.1	1.7	1.7	2.3	5.0
20	α_P	723	116	42	13	19
	α_S	254	59	24	7	3
	α_D	2.8	2.0	1.8	1.9	6.3
30	α_P		180	82	15	23
	α_S	439	95	27	23	11
	α_D		1.9	3.0	0.7	2.1
40	α_P				35	43
	α_S			82	29	17
	α_D				1.2	2.5

4. CONCLUSIONS

From the single liquid sorption experiments it was observed that the solubility of the poly(acrylic acid)–poly(vinyl alcohol) blend membranes could be adjusted by controlling the PAA/PVA ratio in the blends. As the poly(vinyl alcohol) content in the blends increases, the affinity for methanol and ethanol decreases, and thus the solubility of these alcohols decreases. The same dependency of the overall solubility on the blend composition was observed for methanol-toluene and ethanol-toluene mixtures. In addition, for both liquid mixtures the alcohols were preferentially sorbed into the blends and the sorption selectivity increased with increasing amount of poly(vinyl alcohol).

The sorption measurements with methanol-toluene and ethanol-toluene liquid mixtures showed that the varying liquid mixture composition had a strong influence on the overall and preferential sorption. The overall solubility in the poly(acrylic acid)–poly(vinyl alcohol) blends increased very much with increasing alcohol concentration in the liquid mixtures. In contrast, although alcohols were preferentially sorbed over the whole liquid composition range, the sorption selectivity decreased for all tested blends containing poly(vinyl alcohol) 10 to 40 wt.%.

When the contribution of diffusion was evaluated by comparing the pervaporation selectivity with the sorption selectivity, it could be deduced that the preferential sorption dominated the pervaporation selectivity in the studied membrane-liquid mixture systems.

REFERENCES

1. F.W. Greenlaw, R.A. Shelden, and E.V. Thompson, *J. Memb. Sci.*, 2 (1977) 333-348.

2. R. Rautenbach and R. Albrecht, *J. Memb. Sci.*, 25 (1985) 1-23.

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

4. J. Hauser, A. Heintz, G.A. Reinhardt, B. Schmittecker, M. Wesslein, and R.N. Lichtenthaler, "Sorption, Diffusion and Pervaporation of Water/Alcohol Mixtures in PVA-Membranes. Experimental Results and Theoretical Treatment", Proc. of 2nd Int'l. Conf. on Pervapor. Processes in the Chem. Ind., San Antonio, Texas, March 1987. pp. 15-34.

5. P. Aptel, J. Cuny, J. Jozefowicz, G. Morel, J. Néel, and B. Chaufer, *Eur. Polym. J.*, 14 (1978) 595-599.

6. F. Suzuki and K. Onozato, *J. Appl. Polym. Sci.*, 27 (1982) 4229-4238.

7. C. Larchet, G. Bulvestre, and M. Guillou, *J. Memb. Sci.*, 17 (1984) 263-274.

8. M.H.V. Mulder, T. Franken, and C.A. Smolders, *J. Memb. Sci.*, 22 (1985) 155-173.

9. J. Hauser, G.A. Reinhardt, F. Stumm, and A. Heintz, *J. Memb. Sci.*, 47 (1989) 261-276.

10. M.H.V. Mulder, "Thermodynamic Principles of Pervaporation" in: *Pervaporation Membrane Separation Processes*, ed. by R.Y.M. Huang, Elsevier, Amsterdam (1991). pp. 225-251

11. P.J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca,

New York (1953). Chap. 13

12. J.W.F. Spitzen, E. Elsinghorst, M.H.V. Mulder, and C.A. Smolders, "Solution-Diffusion Aspects in the Separation of Ethanol/Water Mixtures with PVA Membranes", Proc. of 2nd Int'l. Conf. on Pervapor. Processes in the Chem. Ind., San Antonio, Texas, March 1987. pp. 209-224

13. J. Gmehling, U. Onken, and J.R. Rarey-Nies (Eds.), *Vapor-Liquid Equilibrium Data Collection: Chemistry Data Series; Vol. 1, Part 2e*, DECHEMA, Frankfurt/Main (1988). p. 370

14. S.N. Kim and K. Kammermeyer, *Separation Sci.*, 5 (1970) 679-697.

15. R.W. Tock, J.Y. Cheung, and R.L. Cook, *Separation Sci.*, 9 (1974) 361.

16. M.H.V. Mulder, T. Franken, and C.A. Smolders, *J. Memb. Sci.*, 23 (1985) 41-58.

Appendix:

Thermodynamic Analysis of Preferential Sorption

Based on the Flory-Huggins thermodynamics of mixing a mathematical model has been derived by Mulder et. al for the description of the preferential sorption phenomena (equation (3) in chapter 4). This equation is very useful for understanding the influence of the factors determining the preferential sorption.

1. Effect of Affinity of Individual Liquids towards the Membrane

The sorption of a binary liquid mixture in a polymer is to a great extent related to the affinity of the components towards the polymer membrane. When the affinity of one liquid is varied while the affinity of the other liquid is kept constant, the preferential sorption will be changed. This effect can be demonstrated by numerical calculations using equation (3) in chapter 4. The results are given in figures 1 and 2. In these calculations all parameters except for the solubility were taken for an ethanol-toluene liquid mixture and a poly(acrylic acid)–poly(vinyl alcohol) (8/2 by wt) blend membrane (see chapter 4). The overall solubility of a binary mixture was assumed to be proportional to the solubilities of single components.

First the influence of the affinity of the more soluble component, liquid 1, on the preferential sorption was investigated (figure 1). In this example, the pure liquid solubility of liquid 1 was varied from 0.5 to 5 g/g[1], while that of the less soluble component, liquid 2, was kept constant at 0.05 g/g. This figure shows that although the liquid 1 solubility increases by up to one order of magnitude the sorption selectivity is hardly influenced. In the second example, however, the pure liquid solubility of liquid 2 was varied from 0.005 to 0.05 g/g, while that of liquid 1 was kept constant at 0.5 g/g (figure 2). From this figure it can be seen that an increasing solubility of the less soluble component has a much larger effect. For instance, a solubility increase from 0.005 to 0.05 g/g for liquid 2 results in a decrease in sorption selectivity of roughly one order of magnitude over the whole feed concentration range.
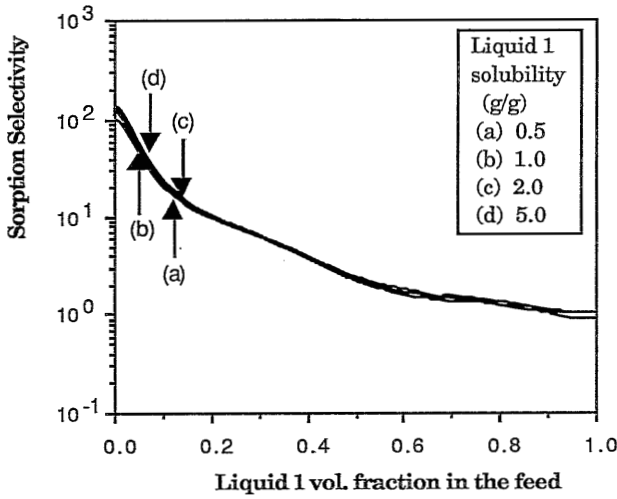
(1) grams of sorbed liquid per gram of dry polymer

Figure 1. Influence of the pure liquid solubility of the more soluble component, liquid 1, on the sorption selectivity. The solubility of the less soluble component is kept constant at 0.05 g/g dry polymer.
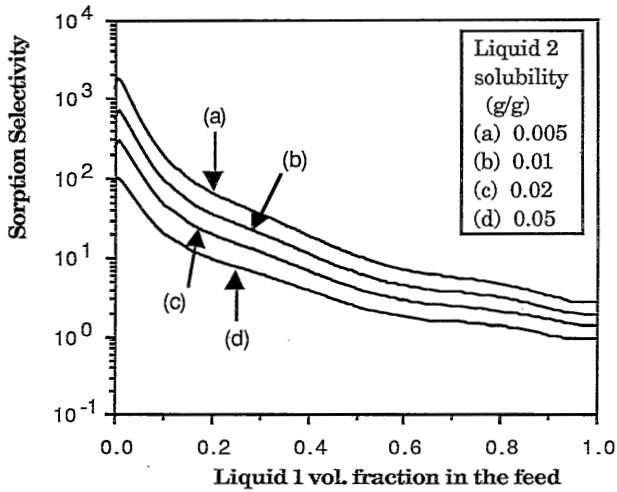

Figure 2. Influence of the pure liquid solubility of the less soluble component, liquid 2, on the sorption selectivity. The solubility of the more soluble component is kept constant at 0.5 g/g dry polymer.

From these calculations it can be concluded that with respect to selectivity it is preferred to decrease the solubility of the less soluble component rather than to increase the solubility of the preferentially soluble component.

2. Overall Sorption versus Preferential Sorption

In the sorption of a binary liquid mixture in a polymer it is quite often observed that as the overall solubility increases the sorption selectivity decreases, or vice versa. This phenomena can also be predicted from the same equation. In these calculations all parameters were also taken for an ethanol-toluene liquid mixture and a poly(acrylic acid)–poly(vinyl alcohol) (8/2 by wt) blend membrane, and these parameters were kept constant. Only ϕ_p, the volume fraction of the polymer membrane, was varied; the overall solubility of a liquid mixture is represented by the overall liquid volume fraction ($= 1 - \phi_p$). The results are given in figure 3. For liquid mixtures with different compositions, the sorption selectivity decreases as the overall liquid volume fraction increases. This clearly confirms a so-called 'trade-off' trend between the overall and preferential sorption. Furthermore a similar phenomenon in permeation, i.e. a decreasing selectivity with an increasing permeability, or vice versa, can be predicted from this calculation.

The effect of crosslinking can also be verified from this result: when a membrane is crosslinked the sorption selectivity increases with a decreasing overall solubility. Under the assumption that the interaction parameter between a solvent and a polymer membrane does not vary with crosslinking, it can be seen from the Flory-Rehner theory that the polymer volume fraction decreases with increasing crosslinking density[2]. The experimental evidence for the decreasing swelling of a membrane with crosslinking is given in chapter 5 of this thesis.

(2) J.W.F. Spitzen, "Pervaporation: Membranes and Models for the Dehydration of Ethanol", Ph.D. thesis, University of Twente, Enschede, The Netherlands (1988). Chap. 2
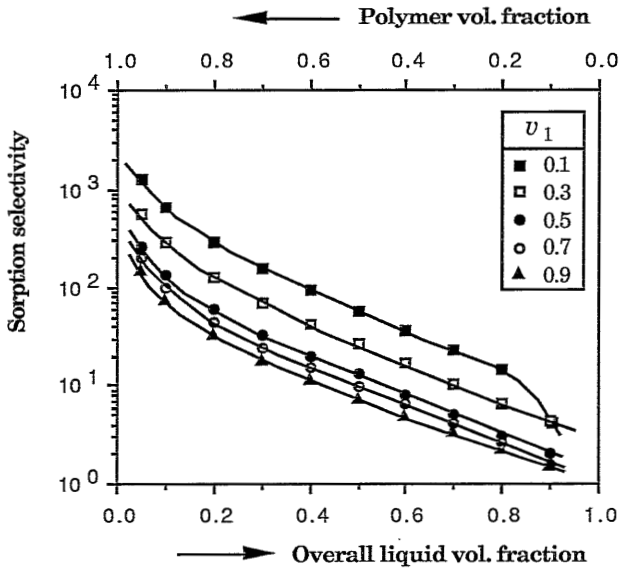
Figure 3. Influence of the polymer volume fraction on the sorption selectivity. The binary interaction parameters between the membrane and the liquid components are kept constant as $\chi_{13} = 0.5828$ and $\chi_{23} = 5.4526$.

Chapter *5*

SEPARATION OF MTBE–METHANOL MIXTURES BY PERVAPORATION

Summary

Membranes made of a polymer blend of poly(acrylic acid) and poly(vinyl alcohol) were evaluated for the separation of methanol from methyl tert-butyl ether by pervaporation. The influence of the blend composition and the feed composition on the pervaporation performance were investigated. Methanol permeates preferentially through all tested blend membranes, and the selectivity increases with increasing poly(vinyl alcohol) content in the blends. However a flux decrease is observed with increasing poly(vinyl alcohol) content. With increasing feed temperature the flux increases, and the selectivity remains constant. In addition, the influence of crosslinking on the permselectivity was investigated. The pervaporation flux decreases with increasing crosslinking density, but the selectivity is enhanced. This is due to a more rapid decrease in the component flux of methyl tert-butyl ether compared to that of methanol.

1. INTRODUCTION

The problem of environmental pollution has urged the reduction of the amount of lead permitted in gasoline, which created a problem of lowering gasoline octane ratings. To maintain the existing quality specifications, octane boosters such as benzene/toluene/xylene mixtures and oxygenates have been added to the lead-free or low-leaded gasoline. Methyl *tert*-butyl ether (MTBE) has been extensively tested and proved to be an octane enhancer. In recent years MTBE is also considered as an oxygenated fuel additive needed to reformulate gasoline which can meet the requirements of the Clean Air Act amendments of USA government. For these reasons the demand for MTBE is increasing rapidly. It has been the fastest growing chemical of the 1980s, and it likely will continue to hold this growth throughout the 1990s [1,2].

Methyl *tert*-butyl ether is produced by a reaction of methanol with iso-butylene in the liquid phase over a strongly acidic ion-exchange resin catalyst. The reaction is rapid and selective, but is limited by equilibrium conditions. Therefore it is desired to improve the conversion by using an excess of methanol. Excess concentrations of methanol up to about 20 % of the stoichiometric amount is generally used to achieve high conversions. The use of excess methanol, however, causes a purification problem because methanol forms minimum-boiling azeotropes with MTBE at a composition of 14.3 wt.% methanol at 760 mmHg. Presently the reactor effluent is first separated by a debutanizer column into a bottom MTBE product and a near-azeotropic mixture of methanol with MTBE at the overhead of the column. Subsequently methanol is washed out by water, and the water/methanol mixture is then distilled to recover methanol for recycle [3,4]. This conventional separation process is both capital and energy intensive.

As an alternative separation technique pervaporation has been considered. It may not be practical to separate completely the entire reactor effluents by pervaporation, but a hybrid distillation-pervaporation process may be very attractive. In this case pervaporation is used only in a limited area of separation such as for breaking the azeotrope. The possibility of a hybrid distillation-pervaporation process can be demonstrated by the Total Recovery Improvement for MTBE (TRIM) process which has been developed by Air Products & Chemicals using cellulose acetate membranes. This process has been developed for both

retrofitting an existing MTBE production plant and replacing the water washing column in a new plant. Laboratory and field-site tests of this process have shown significant energy and cost savings proving that pervaporation is an option to separate methanol from MTBE and light hydrocarbons [5,6].

Farnand and Noh have tested a series of polymers as pervaporation membranes. From the material screening experiments, it was observed that Nafion and a cellulose based material MT showed similar and the best performance among polymers tested [7]. In addition poly(vinyl alcohol) and Nafion have been tested by another research group and also showed a promising result [8,9].

In order to promote industrial acceptance of the pervaporation process, research efforts are aimed to develop membranes with better performance. In this study membranes of a polymer blend of poly(acrylic acid) and poly(vinyl alcohol) are evaluated for the separation of methanol from MTBE by pervaporation. The influence of blend composition and of crosslinking on the permselectivity have been investigated. In addition, the effect of the feed composition and temperature has also been studied.

2. EXPERIMENTAL

2.1. Materials

Poly(acrylic acid) (Mw = 250,000 g/mol) and poly(vinyl alcohol) 96% hydrolyzed (Mw = 85,000 ~ 146,000 g/mol) and 88 % hydrolyzed (Mw = 80,000 ~ 100,000 g/mol) were purchased from Aldrich Chemical Co. Methyl *tert*-butyl ether, methyl alcohol and ethyl alcohol (analytical grade) were obtained from Merck Co. They were used without any further purification. Water was demineralized before use.

2.2. Membrane preparation

Polymer blending was performed by a solution method. Poly(acrylic acid) and poly(vinyl alcohol) were separately dissolved in water. Two solutions were mixed together in various proportions to obtain the proper

casting solutions. Homogeneous membranes were prepared by casting the polymer solution on a Perspex plate with a casting knife. The solvent, water, was slowly removed by evaporation in a flowing nitrogen atmosphere at room temperature. The thickness of the resulting membranes was around 20 μm.

Membrane crosslinking was performed by heat treatment. Membrane samples were first dried for 1 day at 70 °C and then treated at 120 °C for various time intervals in a forced nitrogen convection oven.

2.3. Pervaporation experiments

The pervaporation experiments were performed using the same laboratory test apparatus as previously described in chapter 2 of this thesis. Dry membranes were installed in the pervaporation cells. The effective membrane area in each cell was 50 cm^2. The feed was circulated through the pervaporation cells from a feed reservoir. The feed temperature was kept at 35 °C except for the measurements when temperature was varied. The pressure at the downstream side was kept below 2 mmHg by a vacuum pump. The permeate was collected in cold traps cooled by liquid nitrogen. The composition of the collected permeate was determined by gas chromatography equipped with a thermal conductivity detector.

Pervaporation flux was determined by measuring the weight of liquid collected during a certain time in the cold trap at the steady state. The fluxes of different membranes were normalized to a membrane thickness of 20 μm, assuming a proportionality between the flux and the reciprocal membrane thickness. The pervaporation selectivity α_P is defined by:

$$\alpha_P = (y_1/y_2) / (x_1/x_2) \tag{1}$$

where x and y represent the concentrations in the feed and in the permeate, respectively. Indices 1 and 2 refer to the more permeable component, methanol in this study, and the less permeable one, methyl *tert*-butyl ether, respectively.

3. RESULTS AND DISCUSSION

3.1. Pervaporation through PAA–PVA blend membranes

Membranes made of a polymer blend of poly(acrylic acid) and poly(vinyl alcohol) were evaluated for the separation of methanol from methyl *tert*-butyl ether (MTBE). In previous studies [10, chapter 3 of this thesis], these membranes showed good permselectivities for a similar separation problem, i.e. the separation of methanol and ethanol from mixtures with toluene. Therefore it was expected that these blend membranes would also be good candidates for the separation of methanol from MTBE. Two types of poly(vinyl alcohol) with a degree of hydrolysis of 88 % and of 96 % were used to prepare the polymer blends with poly(acrylic acid). In both cases the PVA content in the blends ranged from 10 to 30 wt.%. The pervaporation results are given in figures 1 and 2 as a function of the PVA content in the blend. For the feed mixtures containing 5 to 20 wt.% methanol the blend membranes of both types of PVA (88 % and 96 % hydrolyzed) showed good separation properties without many differences. As the PVA content increased, the selectivity increased but the flux decreased. The decreasing flux with increasing PVA content is caused by a lower swelling of the blend membranes at a certain feed liquid composition similar as observed in the case of methanol-toluene and ethanol-toluene liquid mixtures (chapter 3 of this thesis).

Figure 3 shows the influence of the feed mixture composition on the permselectivity of blend membranes containing 10 and 20 wt.% PVA of various degrees of hydrolysis. In this figure the flux and selectivity values are presented as a function of the methanol concentration in the feed. As the methanol concentration increases from 5 to 20 wt.%, the selectivity decreases slightly but the flux increases drastically. For example, the blend membrane containing 10 % of 96 % hydrolyzed PVA showed a selectivity decrease from 170 to 45, but a flux increase from 30 to 610 g/m^2h with an increase in the methanol concentration from 5 to 20 wt.%. This increasing flux can be explained in terms of the plasticizing effect exhibited by the permeating molecules. As the methanol concentration in the feed increases, the blend membranes become more swollen due to a strong interaction with methanol. As a result the polymer chains become more flexible, and the resistance for the diffusive transport of penetrants through the membrane becomes less.
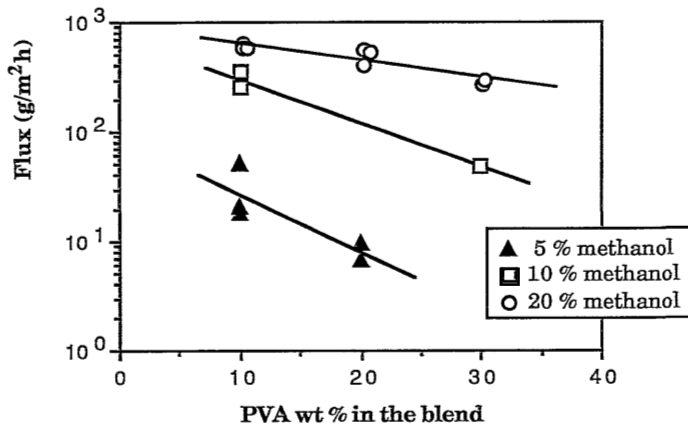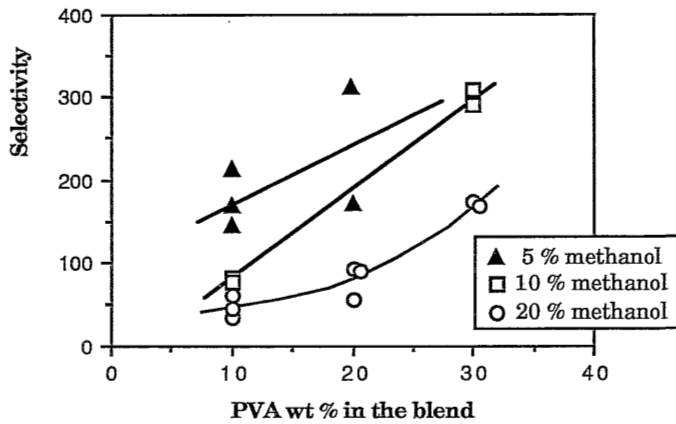
figure 1a

figure 1b

Figure 1. Pervaporation characteristics of blend membranes of PAA with 96 % hydrolyzed PVA for MTBE/methanol liquid mixtures as a function of the blend composition.
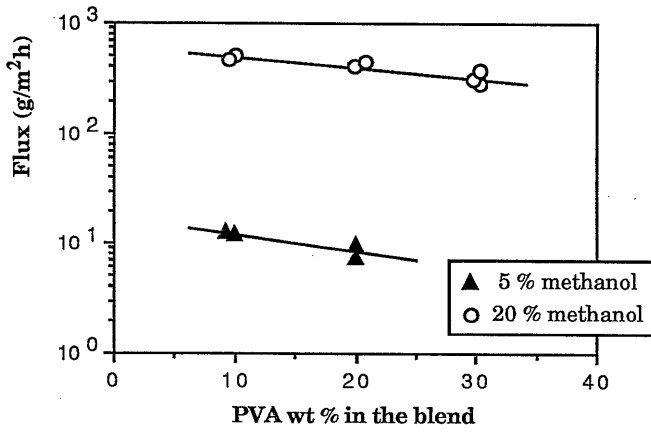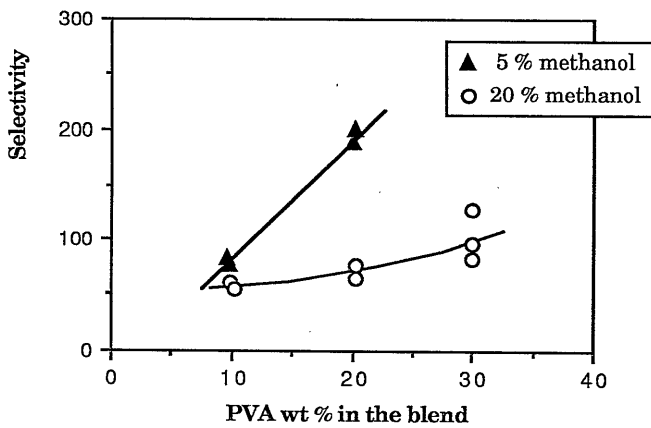
figure 2a

figure 2b

Figure 2. Pervaporation characteristics of blend membranes of PAA with 88 % hydrolyzed PVA for MTBE/methanol liquid mixtures as a function of the blend composition.
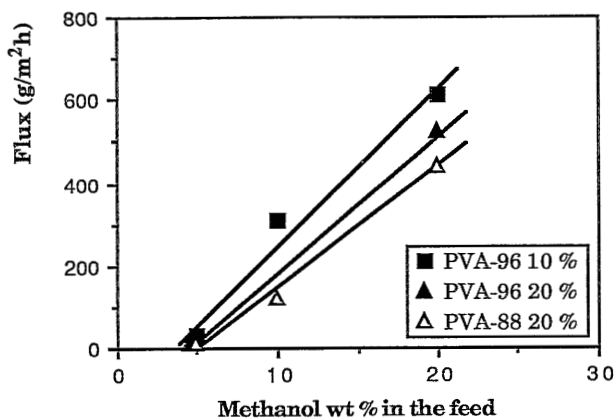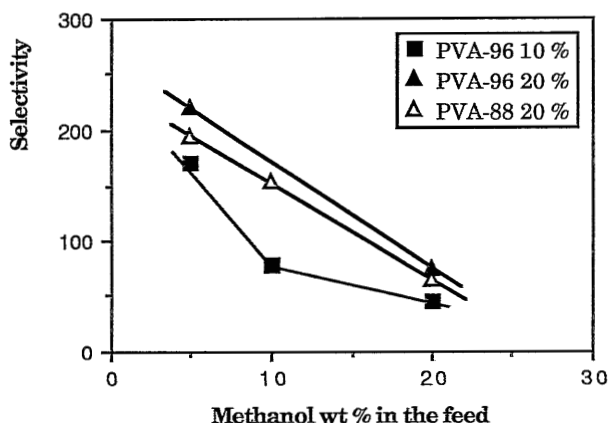
figure 3a

figure 3b

Figure 3. Influence of the feed composition on the pervaporation flux (a) and selectivity (b) of MTBE/methanol liquid mixtures through various PAA–PVA blend membranes.

3.2. Influence of the feed temperature

The temperature dependence of pervaporation has been investigated over a temperature range of 23 ~ 50 °C with a PAA–PVA blend membrane containing 20 wt.% of 88 % hydrolyzed PVA. In figure 4 the pervaporation

flux and selectivity are given as a function of the feed temperature at a feed concentration of 20 wt.% methanol. As it can be seen from the figure, the flux increases gradually with the feed temperature. This can be explained by the enhanced diffusivity with temperature. In pervaporation the dependence of diffusivity on temperature is generally described by an Arrhenius-type exponential relation with the apparent activation energy for diffusion [11,12]. According to this relation diffusivity will increase with temperature when the activation energy is of a positive value, which is mostly observed in the pervaporation of liquid mixtures [13-16]. Besides the enhanced diffusivity, the driving force for the mass transport also increases with temperature. The driving force is given by the difference in partial vapor pressure of the permeants between the feed and the permeate side. As the feed temperature increases the vapor pressure at the feed side increases, while the vapor pressure at the permeate side is not affected. Hence, the driving force increases with temperature.
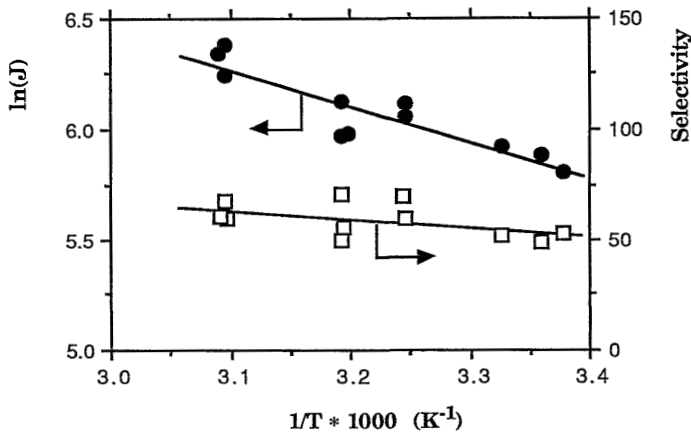

Figure 4. Influence of the feed temperature on flux J (g/m^2h) and selectivity of a PAA–PVA blend membrane for a MTBE/methanol liquid mixture containing 20 wt.% methanol.

Contrary to the flux, the selectivity was hardly affected by a feed temperature ranging from 23 to 50 °C. This indicates that the component fluxes of both methanol and MTBE were influenced to the same extent by the temperature, which can be seen in figure 5. In this figure the total flux

and the component fluxes of methanol and MTBE are presented as a function of the feed temperature. One can see that the slopes of the flux curves are almost equal. In this case the optimal pervaporation performance of the membrane can be obtained at the highest temperature possible.
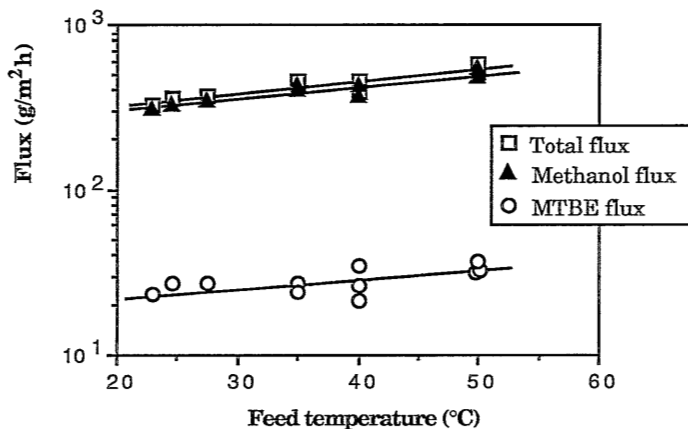

Figure 5. Total flux and component fluxes of methanol and MTBE through a PAA–PVA blend membrane as a function of the feed temperature.

3.3. Crosslinked membranes

There is a growing interest in the improvement of the separation properties of a membrane by crosslinking. As a polymer membrane is crosslinked, the solubility of a liquid feed in the membrane is reduced, as can be deduced from the Flory-Rehner theory [17], see equation (2). From the Flory-Huggins thermodynamics for mixing it can be seen that the sorption selectivity increases with decreasing overall solubility (see appendix in chapter 4). Crosslinking also reduces the mobility of the polymer segments and thus reduces the diffusivity of penetrants through a membrane. For instance, the diffusion coefficient of nitrogen in natural rubber is reported to be reduced tenfold upon crosslinking the rubber with 11 % sulfur [18]. The reduced diffusivity as well as the reduced solubility might cause a decrease in pervaporation flux but an increase in selectivity.

The PAA–PVA blend membranes were crosslinked by a heat treatment at 120 °C. This crosslinking temperature was experimentally determined to work satisfactorily. When the blend membranes were treated for two hours at higher temperatures, for example at 140 °C, the crosslinked membranes showed extremely low fluxes for the methanol-MTBE mixtures at 20 wt.% methanol. Therefore it was decided to perform the heat treatments at 120 °C for a better control of crosslinking density.

Although the crosslinking mechanism is not identified, it probably occurs through an esterification reaction. The carboxyl functionality of PAA can react with the hydroxyl functionality of PVA resulting in an ester linkage by the elimination of water. An esterification reaction has been used already to crosslink PVA with diacids; this is comparable with the PAA–PVA system [19].

A blend membrane of poly(acrylic acid) and 88 % hydrolyzed poly(vinyl alcohol) containing 20 wt.% PVA was heat-treated over various periods of time. To determine the crosslinking density the equilibrium solubility of pure ethanol at room temperature was measured. The sorption results are given in table 1. As the time of the heat treatment increases, the solubility of ethanol decreases rapidly. When the membrane was treated for 16 hours it was hardly swollen by ethanol. From this result it appears that the blend membranes can be crosslinked by a heat treatment and that the crosslinking density can be controlled by adjusting the heating time.

The crosslinking density or molecular weight between two adjacent crosslinks can be calculated from the Flory-Rehner theory [18]. According to this theory the chemical potential of a solvent $\Delta\mu_i$ in a polymer is given as a function of the volume fraction of the polymer ϕ_p:

$$\Delta\mu_i/RT = \ln(1 - \phi_p) + \phi_p + \chi_{ip}\phi_p^2 + (\rho V_i/M_c)(\phi_p^{1/3} - \phi_p/2) \qquad (2)$$

where ρ and M_c are the density of dry polymer and the molecular weight between two adjacent crosslinks, respectively. V_i is the molar volume of the solvent. The last term at the right hand side of the above equation represents the contribution of the elastic effect. At swelling equilibrium $\Delta\mu_i/RT = 0$. The volume fraction of the polymer ϕ_p can be determined from an equilibrium sorption experiment. Therefore when the M_c value is known the binary interaction parameter χ_{ip} can be calculated from equation (2), or vice versa.

In the case of sorption into the uncrosslinked blend membrane the elastic term can be neglected compared to the first three terms. In such a situation the binary interaction parameter χ_{ip} can be calculated from equation (2) using the experimental volume fraction of the membrane ϕ_p. A value of 0.5728 was calculated for the interaction parameter between ethanol and the uncrosslinked PAA–PVA blend membrane. For the calculation of M_c, the molecular weight between two adjacent crosslinks, it was assumed that the interaction parameter between ethanol and the blend membranes did not vary with crosslinking. This means that the interaction parameter calculated for the uncrosslinked membrane is equally valid for the crosslinked membranes. The calculated M_c values under this assumption are given in table 1. As the crosslinking time increases, the ethanol solubility decreases drastically which is also expressed by a smaller M_c value indicating a higher crosslinking density. However the numerical values of M_c are unrealistically low, which may be due to the assumption of a constant interaction parameter. Nevertheless this result confirms clearly that the PAA–PVA membrane can be crosslinked by a heat treatment and the crosslinking density can be controlled by adjusting the heating time.

Table 1. *The solubility of ethanol in the crosslinked PAA–PVA blend membranes (PVA content of 20 wt.%) at room temperature and the molecular weight between two adjacent crosslinks M_c, calculated from equation (2).*

crosslinking time at 120 °C (hr)	ethanol solubility (g/g)	polymer volume fraction	binary interaction parameter	M_c (g/mol)
0	2.43	0.1875	0.5728	—
2	1.78	0.2395	—	29,000
5	0.26	0.6832	—	220
7	0.10	0.8486	—	70
16	0	1	—	—

* density of the blend = 1.40 g/cm^3

The influence of crosslinking on the pervaporation flux and selectivity was investigated using the blend membrane of 88 % hydrolyzed PVA (20 wt.% in the blend). The results are presented in figure 6 for a methanol-MTBE mixture containing 20 wt.% methanol. This figure shows that the flux decreases but the selectivity increases with increasing crosslinking time. This can be explained by the reduced solubility and diffusivity as discussed before.

The improvement of the separation factor is caused by a more rapid decrease of the MTBE flux compared to methanol (figure 7). In the crosslinking time interval of 0 to 7 hours the methanol component flux shows a rather linear decrease, but the decrease of MTBE component flux shows a more concave curve. This can be due to the different molecular sizes of the permeants. The molar volumes of methanol and MTBE are 40.73 and 119.04 cm^3/mol, respectively, at 25 °C. Therefore with even the same reduction in the polymer chain flexibility, the larger molecule of MTBE should experience a larger frictional force in diffusion than the smaller methanol molecule.
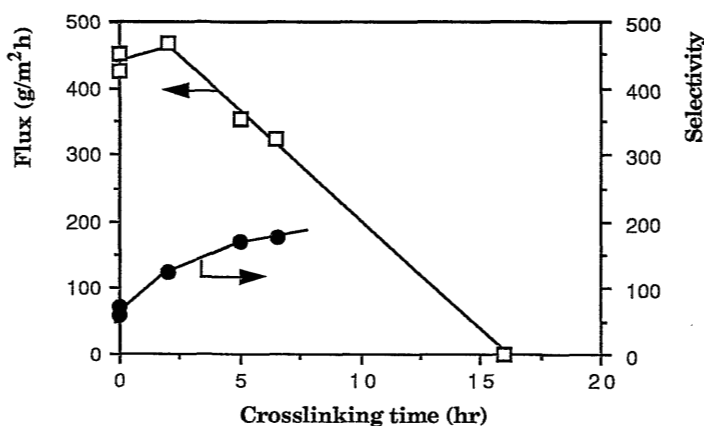

Figure 6. Influence of membrane crosslinking on pervaporation flux and selectivity of a PAA–PVA blend membrane (20 % PVA) for a methanol-MTBE liquid mixture containing methanol 20 wt.%, as a function of the crosslinking time.
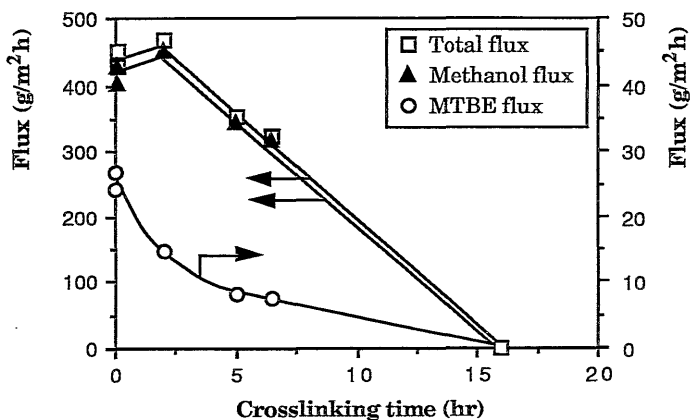
Figure 7. Total flux and component fluxes of methanol and MTBE through the crosslinked PAA–PVA blend membranes, as a function of the crosslinking time.

4. CONCLUSIONS

Membranes of a polymer blend of poly(acrylic acid) and poly(vinyl alcohol) were evaluated for the separation of methanol from methyl *tert*-butyl ether. For feed mixtures of 5 to 20 wt.% methanol, the blend membranes containing 10 to 30 wt.% PVA showed both high fluxes and high selectivities. Furthermore it was observed that the separation characteristics of the blend membrane could easily be controlled by adjusting the blend composition. As the poly(vinyl alcohol) content in the blends increased, fluxes decreased gradually but selectivities increased. In addition, a strong influence of the feed mixture composition on the separation characteristics was also observed.

The temperature of the feed liquid showed a favorable effect on the separation performance of the system studied. The flux increased with temperature, while the selectivity was hardly affected. This implies that an optimal pervaporation performance can be obtained at the highest temperature possible.

By crosslinking the membranes the flux decreases, but the selectivity increases. From the comparison of the component fluxes it appeared that the MTBE flux was more reduced compared to that of methanol.

REFERENCES .

1. G. Pecci and T. Floris, "Ethers Ups Antiknock of Gasoline", *Hydrocarbon Processing*, 56(12) (Dec. 1977) 98-102.

2. S.J. Ainsworth, "Booming MTBE Demand Draws Increasing Number of Producers", *Chemical & Engineering News*, June 10, 1991, pp. 13-16.

3. J.D. Chase, "Synthesis of High Octane Ethers from Methanol and Iso-Olefins" in: *Catalytic Conversion of Synthesis Gas and Alcohols to Chemicals*, ed. by R.G. Herman, Plenum, New York (1984). p. 307

4. L.S. Bitar, E.A. Hazbun, and W.J. Piel, "MTBE Production and Economics", *Hydrocarbon Processing*, 63(10) (Oct. 1984) 63-66.

5. M.S. Chen, R.M. Eng, J.L. Glazer, and C.G. Wensley, "Pervaporation Process for Separating Alcohols from Ethers", US Pat. 4,774,365 (1988).

6. M.S.K. Chen, G.S. Markiewicz, and K.G. Venugopal, "Development of Membrane Pervaporation TRIM™ Process for Methanol Recovery from $CH_3OH/MTBE/C4$ Mixtures", *AIChE Symp. Ser.*, 85(272) (1989) 82–88.

7. B.A. Farnand and S.H. Noh, "Pervaporation as an Alternative Process for the Separation of Methanol from C4 Hydrocarbons in the Production of MTBE and TAME", *AIChE Symp. Ser.*, 85(272) (1989) 89–92.

8. M. Pasternak, C.R. Bartels, and J. Reale, Jr., "Separation of Organic Liquids", US Pat. 4,798,674 (1989).

9. V.M. Shah, C.R. Bartels, M. Pasternak, and J. Reale, "Opportunities for Membranes in the Production of Octane Enhancers", *AIChE Symp. Ser.*, 85(272) (1989) 93–97.

10. H.C. Park, R.M. Meertens, M.H.V. Mulder, and C.A. Smolders, "Pervaporation of ethanol-toluene mixtures", *Membraantechnologie*, 5 (1990) 27.

11. T. deV. Naylor, "Permeation Properties" in: *Comprehensive Polymer Science, Vol. 2: Polymer Properties*, ed. by C. Booth and C. Price, Pergamon Press, Oxford (1989). pp. 643-668

12. T.M. Aminabhavi, U.S. Aithal, and S.S. Shukla, *J. Macromol. Sci. - Rev. Macromol. Chem. Phys.*, C28(3&4) (1988) 421-474.

13. I. Cabasso, J. Jagur-Grodzinski, and D. Vofsi, *J. Appl. Polym. Sci.*, 18 (1974) 2137-2147.

14. R.Y.M. Huang and and N.R. Jarvis, *J. Appl. Polym. Sci.*, 14 (1970) 2341-2356.

15. E. Nagy, J. Stelmaszek, and A. Ujhidy, "Separation of Benzene-Methanol and Benzene-Cyclohexane Mixtures by Pervaporation Process" in: *Membranes and Membrane Processes*, ed. by E. Drioli and M. Nakagaki, Plenum Press, New York (1986). pp. 563-571

16. E. Ruckenstein and J.S. Park, *J. Appl. Polym. Sci.*, 40 (1990) 213-220.

17. P.J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York (1953). Chap. 13

18. R.M. Barrer and G. Skirrow, *J. Polym. Sci.*, 3 (1948) 549.

19. H. Bruschke, "Mehrschichtige Membran und ihre Verwendung zur Trennung von Flüssigkeitsgemischen nach dem Pervaporationsverfahren", German Pat. DE 3220570 (1983).

Appendix:

Effect of Membrane Pre-conditioning

The permeation property of a glassy polymer membrane can be influenced by pre-conditioning. Jordan et. al have already shown that the permeability of a polycarbonate membrane for various gases can be improved very much by pre-conditioning the membrane with CO_2 at high pressure [A1]. Pre-conditioning may also strongly affect the pervaporation property of a glassy polymer membrane for a liquid mixture.

A blend membrane of poly(acrylic acid) and poly(vinyl alcohol) containing 30 wt.% PVA was pre-conditioned in methanol-MTBE mixtures with various compositions before performing a pervaporation experiment. The blend is in the glassy state as has been proved from the glass transition temperature measurements (see chapter 3 of this thesis). The pervaporation results of this blend for a methanol-MTBE (1/9 by wt) mixture at 35 °C are given in figures 1 and 2. A membrane which was swollen in a liquid mixture containing 10 wt.% methanol showed the same flux as a membrane which was not pre-conditioned. However, when membranes were swollen in liquid mixtures containing more methanol, i.e. 30 and 50 wt.%, much higher fluxes were obtained. Furthermore the flux increases with increasing methanol content in the pre-conditioning liquid. The flux decreases with the pervaporation time, but more rapidly for a more swollen membrane. However, it can be seen from figure 1 that
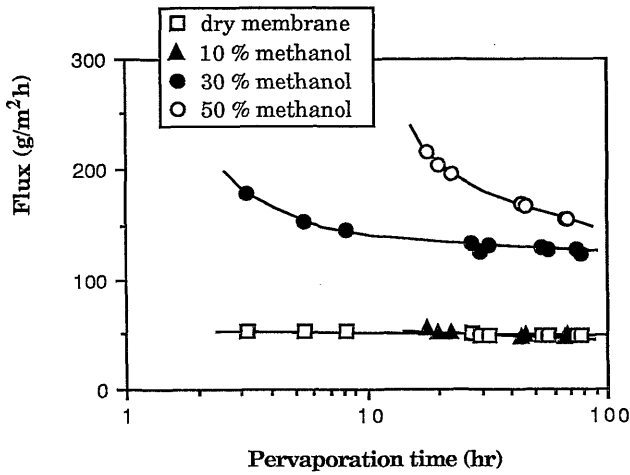
Figure A1. Influence of membrane pre-conditioning on the pervaporation flux of a methanol-MTBE (1/9 by wt) mixture through a PAA–PVA blend (30 % PVA) membrane, as a function of the pervaporation time.
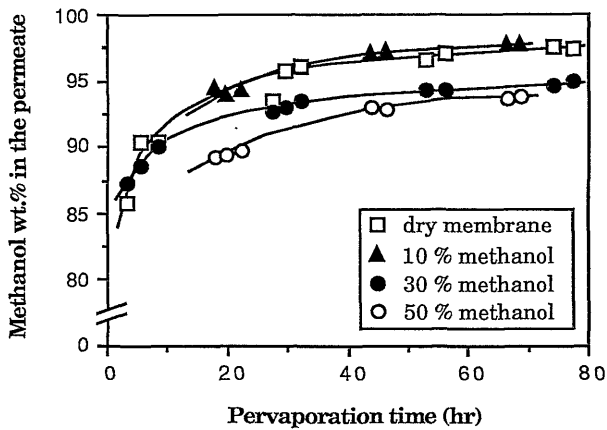

Figure A2. Influence of membrane pre-conditioning on the methanol concentration in the permeate for the pervaporation of a methanol-MTBE (1/9 by wt) mixture through a PAA–PVA blend (30 % PVA) membrane, as a function of the pervaporation time.

it will take a quite long time until the fluxes of more swollen membranes approach to that of a dry membrane.

The different pre-conditioning shows also a strong effect on the permeate composition. When a membrane is swollen in the feed, the methanol concentration in the permeate is almost the same as obtained with a dry membrane. However membranes which are swollen in liquid mixtures containing 30 and 50 wt.% methanol show a lower methanol concentration in the permeate.

The pre-conditioning effect seems to be related to subtle morphological alterations of a glassy polymer matrix. For more detailed information the reader is referred to the literature [A2].

References

A1.   S.M. Jordan, W.J. Koros, and G.K. Fleming, J. Memb. Sci., 30 (1987) 191-212.

A2.   M. Wessling, "Relaxation Phenomena in Dense Gas Separation Membranes", Ph.D. thesis, University of Twente, Enschede, The Netherlands (1993).

SUMMARY

In the chemical industry, distillation is generally the preferred technique to separate a liquid mixture. However some liquid mixtures such as azeotropic mixtures, close-boiling hydrocarbons, and various isomers are difficult to separate by simple distillation. For the separation of these mixtures normally techniques like extractive or azeotropic distillation and liquid-liquid extraction are used. The relatively high energy consumption for these processes has encouraged the development of new, less energy-consuming separation processes such as pervaporation.

In recent years, the pervaporation process was actively studied for the separation of organic-organic liquid mixtures. This may be considered as a major application area for pervaporation in the chemical processing industry.

In this thesis, the separation of alcohols from non-polar solvents like toluene and methyl *tert*-butyl ether by pervaporation is discussed. The main objective of research is the development of new membrane materials with a good permselectivity. For the selective removal of alcohols, the membrane materials must be able to interact preferentially with alcohols. In the beginning commercially available polymers have been selected, which are polar and can form hydrogen bonds with alcohols. These polymers were tested on separation performance for an ethanol-toluene mixture (chapter 2).

New 'tailor-made' materials can be developed for specific applications by (a) synthesis of new polymers, (b) modification of existing polymers, and (c) polymer blending. In chapter 3 the polymer blending method is applied to develop specific membrane materials. Using this method it is possible to produce a range of materials with properties in between or completely different from those of constituting polymers. An obvious advantage of this approach is the low development costs. Based on this approach a homogeneous blend membrane of poly(acrylic acid) and poly(vinyl alcohol) has been selected. From the pervaporation experiments with alcohol/toluene mixtures it is observed that the polymer blending method can give optimal membranes for this type of separation. The performance can easily be adjusted by varying the ratio of the two homo-polymers: with increasing poly(vinyl alcohol) content the pervaporation selectivity increases, but the flux decreases.

The feed mixture composition shows a strong influence on the permselectivity. The flux increases drastically with increasing alcohol concentration in the feed for all blend membranes tested, whereas the selectivity decreases. The component flux of toluene is to a large extent affected by the presence of alcohol. The toluene flux increases while its concentration decreases from 90 to 30 wt.% in the feed. This might be due to the increased sorption in the membranes which are plasticized by the alcoholic component.

The solution part of the solution-diffusion mechanism is described in chapter 4. The overall and preferential sorption of methanol-toluene and ethanol-toluene liquid mixtures in the blends of poly(acrylic acid) and poly(vinyl alcohol) were determined and compared with the pervaporation results. As the poly(vinyl alcohol) content in the blend increases, the overall solubility decreases but the sorption selectivity increases. This indicates that the similar trend observed from the pervaporation experiments; i.e. an increase in flux but a decrease in selectivity with increasing poly(vinyl alcohol) content, is related to the sorption characteristics. In addition, a clear relation between the pervaporation flux and the overall solubility is observed. A comparison of the pervaporation and sorption selectivity shows that the preferential sorption is a leading factor for selective transport in pervaporation.

The preferential sorption is predicted by a model which is derived from Flory-Huggins thermodynamics. This model is proved to be very useful for understanding the influence of governing factors for the preferential sorption. Using a pure toluene solubility of 0.01 g/100 g dry membrane, the composition of the sorbed liquids can be quantitatively predicted. From numerical calculations, the importance of a lower solubility of the less soluble component is illustrated. An increasing selectivity with decreasing overall solubility can also be verified.

In chapter 5 the selective separation of methanol from methyl *tert*-butyl ether by pervaporation is presented. Since methanol forms an azeotrope with methyl *tert*-butyl ether, this is difficult to separate by the conventional distillation process. The pervaporation experiments with a blend membrane of poly(acrylic acid) and poly(vinyl alcohol) shows that methanol permeates preferentially and the selectivity increases with increasing poly(vinyl alcohol) content. The selectivity can be further improved by crosslinking, but at the expense of permeability.

Curriculum Vitae

Hyun-Chae Park was born on December 29, 1959 at Kimhae, Korea. He graduated at the Masan High School in 1978 and entered the Seoul National University, Korea in the next year, 1979. There he studied at the Department of Chemical Technology for four years and took his bachelor's degree in March 1983. He continued his study at the same department as a graduate student. After graduation with a M.Sc. degree in Engineering in 1985 he served in the Korean Army for six months. At the Korea Advanced Institute of Science and Technology where he worked for two years he carried out a research project on membrane technology. It was his first experience in the membrane field. In November 1988 he came over to the Netherlands and started his study in the Membrane Technology Group supervised by Prof. Smolders at the University of Twente. The research topic was the separation of organic liquid mixtures by pervaporation. He finishes his four year study at the University of Twente with a Ph.D. degree on January 7, 1993.