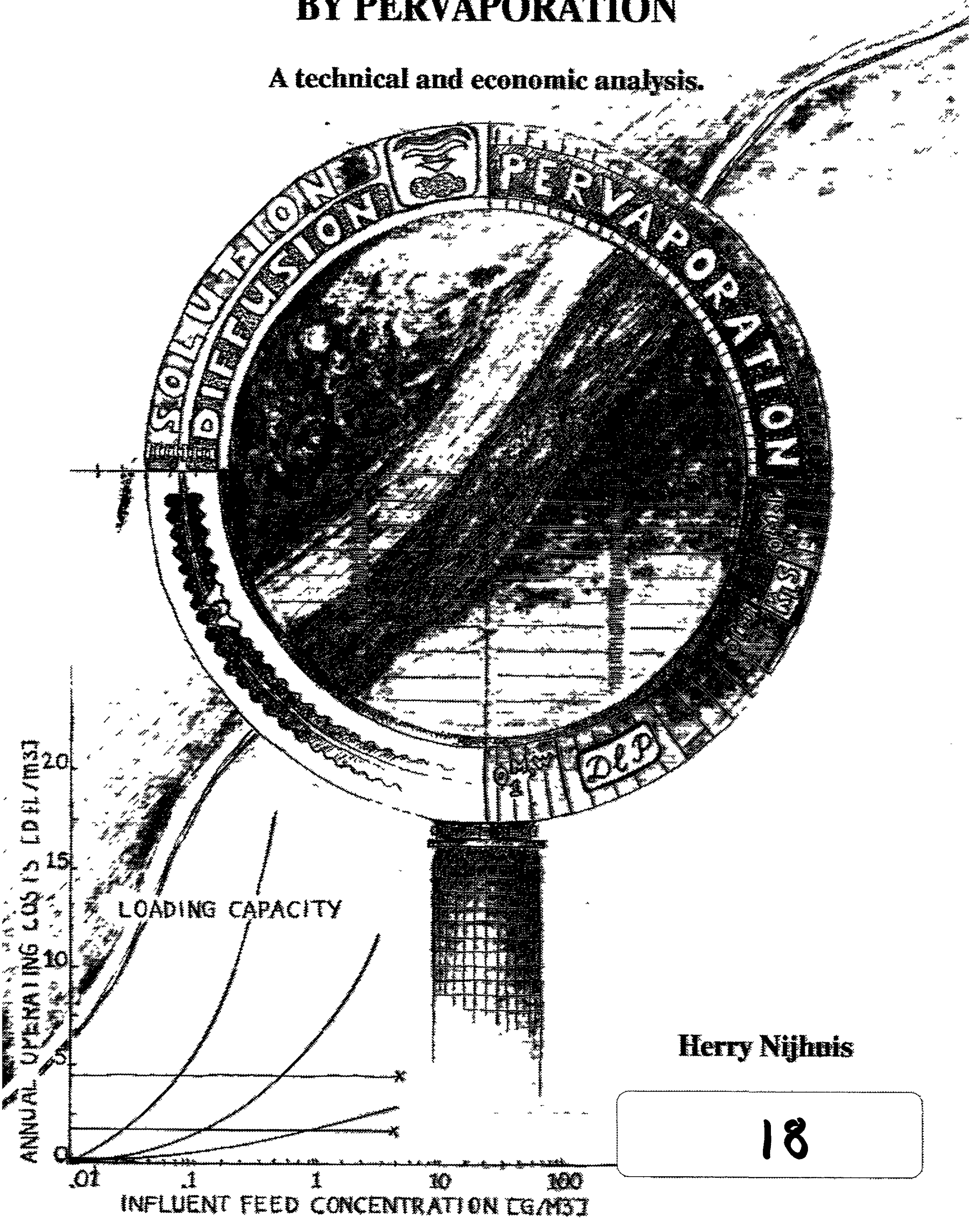
REMOVAL OF TRACE ORGANICS FROM WATER BY PERVAPORATION

A technical and economic analysis.



Herry Nijhuis

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REMOVAL OF TRACE ORGANICS FROM WATER BY PERVAPORATION

A technical and economic analysis

PROEFSCHRIFT

ter verkrijging van
de graad van doctor aan de Universiteit Twente,
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volgens het besluit van het College van Dekanen
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door

HERMAN HENK NIJHUIS
geboren op 7 september 1959
te Hengelo (O)

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Assistent promotor: dr. ing. M.H.V. Mulder
Referent: dr. M.C.H. van Drunen

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VOORWOORD

Op deze plaats wil ik allen hartelijk danken die mijn verblijf op 'Chemische Technologie' tot een tijd hebben gemaakt, waarop ik nog lang met veel plezier zal terugkijken. In de eerste plaats de directe collega's die de afgelopen (bijna) vijf jaar een bijzonder prettig werkklimaat wisten te creëren. Daarnaast echter ook de mensen die achter de schermen hebben gewerkt en indirect bij het onderzoek betrokken zijn geweest. Met name de hulp van de mensen uit de glasinstrumentmakerij en het apparatencentrum is vaak onontbeerlijk geweest.

Een belangrijke rol bij het vergaren van de experimentele resultaten was weggelegd voor een aantal assistenten, stagiaires en afstudeerders. Annemarie, Erik, Hjalmar, Rik en Mike en de vele 2.3 praktikanten hebben allen op hun eigen wijze bijgedragen tot de totstandkoming van dit proefschrift. Ronny Bosch wil ik graag met name noemen. In het jaar dat hij binnen onze groep werkzaam is geweest, heeft hij voor veel nuttige meetresultaten gezorgd. Zandrie was er om de laatste experimentele puntjes op de i te zetten.

In de laatste fase van het onderzoek heb ik veel steun gehad van mijn kamergenoten Geert-Henk, Hyun Chae en Petrus, die mij telkens weer door moeilijke momenten wisten heen te sleuren. Dr. M.C.H. van Drunen heeft een belangrijke bijdrage geleverd bij het tot stand komen van de economische evaluatie, terwijl Ingo Blume een onuitputtelijke bron van 'pervapkennis' bleek te zijn en zijn steen(tje) heeft bijgedragen bij de eerste correcties. Marcel Mulder en Kees Smolders hebben mij in wetenschappelijke zin gesteund om het een en ander op een nette manier op papier te krijgen. Tevens hebben zij ervoor gezorgd, dat ik bij gelegenheid de resulaten van het verrichte onderzoek in binnen- en buitenland heb mogen presenteren. De steun die ik van Marcel Mulder tijdens het onderzoek gehad heb, met name in de laatste kritische fase, is voor mij van grote betekenis geweest.

27 september 1990

Herry

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CHAPTER 1

MEMBRANES IN ENVIRONMENTAL APPLICATIONS

H.H. Nijhuis

1.1 INTRODUCTION

Can membranes help to solve the environmental problems, which have been caused by mankind ever since the beginning of the industrial revolution, within a relatively limited period of time? This is the major question to be answered in this chapter. When in 1980 the pollution at the location 'Lekkerkerk' in the western part of the Netherlands came to light, nobody could foresee the extent to which these environmental problems would increase. The national institute for public health and environmental care (RIVM) indicated already in 1985, that at the end of this century 1400 small and 60 large soil sanitation projects should be rounded off. This involves 13 million m^3 of contaminated soil of which 5.5 million m^3 actually must be cleaned [1]. The Dutch government has earmarked 2.4 billion guilders for soil sanitation until 1997 [2]. An estimated amount of 25 billion guilders will probably be required for complete sanitation of all the factory sites in our country [3].

Although an environmental market as such does not really exist, several partial markets can be distinguished as indicated in table 1 [4]. From this table it may be concluded that the market for environmental equipment is growing more rapidly than has been estimated on forehand. This general tendency of unpredictable, rapid growth makes it very difficult to estimate the market situation in the near future, but it seems justified to conclude that at least the prospects are good.

The severe pollution cases which came to light have accelerated new developments in the field of soil sanitation technologies. Several Dutch companies have built up a strong position in this field. The government supports these developments financially (the so called Stimuleringsregeling Milieutechnologie; SMT), which strengthens the good position of our national environmental industry. Illustrated by the large number of reports written, the governmental policy and the environmental legislation, the necessity for sanitation and prevention of further contamination of the soil is clear for everybody. In this chapter a short review of the soil sanitation techniques will be presented with special focus on membrane processes in general and pervaporation in particular.

Table 1: Overview of the Dutch environmental market [4]

PARTIAL MARKET	**TURNOVER**			**ESTIMATED TURNOVER IN 1990**	
	1981	**1982**	**1985**	**vision '83**	**vision '85**
		[in M Dfl]		**[in M Dfl]**	
water purification	490	630	670	505	700
air pollution	115	175	615	305	750
soil sanitation	-	-	145	-	250
non-chemical wastes	105	160	300	140	450
chemical wastes	15	25	30	60	150
others	75	110	240	160	300
TOTAL	800	1,100	2,000	1,170	2,600

1.2 SOIL SANITATION TECHNOLOGIES

The large multinationals are often directly connected with contaminated sites. There are, however, several other branches of industry that are suspect on forehand:

- paint production and usage
- galvanic industry
- pesticide production
- chemical dry-cleaning
- printing industry
- gas-works.

As a result of irresponsible handling, whether wittingly or not, chemical substances, either raw materials, products or chemical wastes have vanished into the soil. These chemical substances can be inorganic contaminants, i.e. heavy metals, (complexated) cyanides and ammonia, or organic substances. The main organic pollutants are (polycyclic) aromatics, phenols, alifatics, volatile and non volatile halogenated hydrocarbons. In table 2 the contaminated sites and the extent of pollution have been summarized according to the kind of major pollutant [5].

Table 2: Survey of contaminated sites and their extents in the Netherlands [5]

CONTAMINANTS	EXTENT [m^3]	[%]
Alifatics and aromatics	1,430,000	(42%)
Polycyclic aromatics	220,000	(6.5%)
Cyanides	270,000	(8%)
Volatile chlorinated hydrocarbons	340,000	(10%)
Non-volatile chlorinated hydrocarbons	170,000	(5%)
Heavy metals	970,000	(28.5%)
TOTAL	**3,400,000**	**(100 %)**

Several sanitation technologies are available to treat the contaminated soil: They can be divided into four categories:

- thermal treatment
- extraction
- biological treatment
- isolation

The first three technologies can actually clean the soil, whereas isolation merely aims at preventing further contamination of the soil and the ground water, and thus reducing the effects on the public health. In figure 1 a complete flow scheme for soil and ground water sanitation is schematically presented. In the following sections the principles of the four technologies will be summarized. For a more extensive overview of soil sanitation technologies one is referred to literature sources [6, 7].

Thermal treatment

The contaminants are removed from the soil by a heat treatment. After the ground has been excavated this can be established off-site in a process unit, which is heated either by direct contact with hot air or indirectly through heat exchangers. In the case of cleaning in situ heat is added to the ground either via steam or hot air [8]. The pollutants are transferred to the vapor phase, rise to the surface where they are collected and aftertreated if necessary. In the Netherlands 11 installations are in operation, which can incinerate chemical and domestic wastes as well as contaminated soil. Recent developments in this field aim at removing the contaminants in a less severe way in order to reuse the cleaned ground.

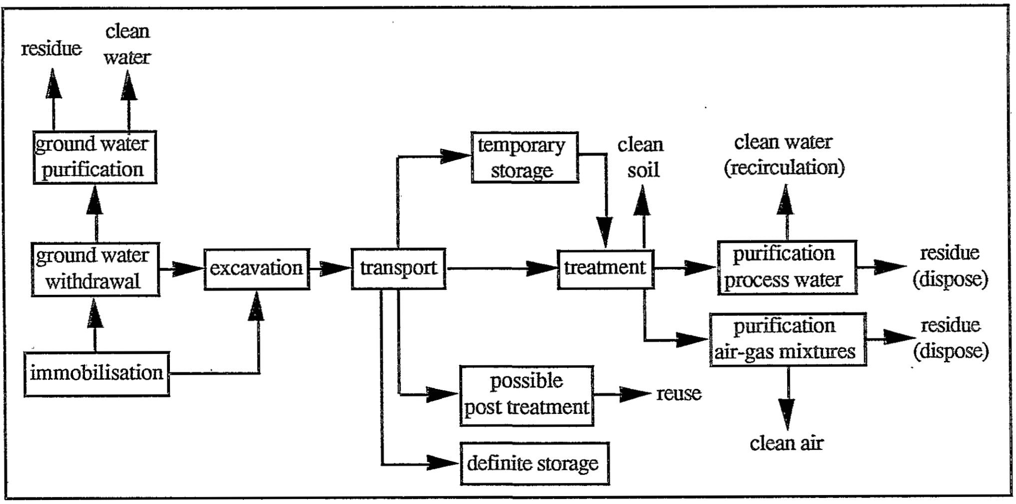


Figure 1: Systems for the sanitation of soil and ground water

Extraction

Extraction is a process in which a liquid is involved to 'wash' the ground. The liquid will in most cases simply be water to which generally chemicals (e.g. detergents) are added to increase process performance. The most critical steps in the extraction process are the thorough mixing and separation of ground and liquids and the purification of the contaminated extraction fluid. Extraction is a well established large scale industrial process. This implies that already several types of apparatuses are commercially available, which accelerated the development of this process.

Biological treatment

In biological treatment systems contaminants are degraded through biological activity. After excavation, the contaminated soil is cleaned off-site in either a so-called 'landfarming' or a composting process. In the latter process a higher amount of organic material is involved. Biological treatment in situ is possible through a landfarming process for contaminants present upto a depth of one meter.

Micro organisms, which adapted themselves over the years to a lot of media, play an essential role in this process. In principle each organic substance can be degraded by means of enzymatic systems or by micro organisms containing the essential enzymes. These enzymes are produced by a large number of small mutations, only when the micro organisms have been in contact with the contaminants for a sufficiently long time. For several components in mineral oil these mutations have already been executed in situ, whereas bacterial enzymes are able to convert chlorinated hydrocarbons, polycyclic aromatics and pesticides. It seems that there are no fundamental problems to degrade contaminating substances via biological means. Low conversion rates are observed for chlorinated hydrocarbons, PCB's, HCH and polycyclic aromatics due to:

- contact limitations of micro organisms and contaminants
- growth limitations of micro organisms by the deficiency of nutrients
- growth limitations of micro organisms through toxic substances
- conversion limitations through external factors, like humidity, temperature and the presence of other organisms.

Summarizing it can be stated that microbiological sanitation processes are able to actually clean the soil [9]. The organic substances already present are preserved in contrast to thermal treatment, whereas the quantity of waste products is minor compared to extraction processes. On economic grounds a biological sanitation procedure should also be preferred. A clear disadvantage of biological treatment is the often low efficiency and the long sanitation time. For sanitation in situ it is therefore essential to prevent emissions to the surroundings, by isolating the contaminated area.

Isolation

Isolation techniques aim at preventing migration of the contaminants to the surroundings without removing the source of the pollution. Isolation techniques can be divided into three main groups:

- civil-technical isolation, where a barrier is placed to stop the emission
- geohydrological isolation, by which contaminated ground water is pumped up via an installed ground water withdrawal system
- physico-chemical isolation, by which through injection of chemicals the contaminants are immobilized.

In civil-technical isolation horizontal and vertical methods can be distinguished. Horizontal isolation methods include the coverage of the contaminated site as well as the introduction of an impermeable layer under the contaminated site. With respect to the high cost civil-technical isolation is often restricted to installation of vertical screens or to the introduction of an impermeable layer on top of a site, when by nature an impermeable layer is already present somewhere in the soil below the contaminants.

Geohydrological isolation has in principle not the intention to treat the withdrawn ground water. If, however, this technique is combined with a water purification system it can be considered as an in situ sanitation process.

Application of physico-chemical isolation is restricted to cases where with respect to the future destination of the site and the kind of pollutants, a definite removal is not required. Especially in cases where an impermeable layer is present only at great depths, immobilization of the contaminants can be a useful alternative.

A ground water withdrawal installation is a strict requirement in combination with isolation to induce an inwards flow from the surroundings into the contaminated area instead of a contaminating flow outwards. The waste water stream thus produced has to be purified in most cases before drainage to the sewer or to the surface water. Besides the cost for purification of the waste water, the operating costs (labour, maintenance, repair and replacement at the end of the lifetime of the system) should also be taken into account. For small contaminated sites this will imply a decision to actually clean the soil instead of wrapping it up. For extremely large scale operations for which no suitable treatment technology is available yet, the decision to isolate the contaminated area may be justified.

1.3 GROUND WATER PURIFICATION

Because of the high cost, the excavation and treatment of the contaminated soil off site should be limited as much as possible especially for large operations. Therefore in situ techniques, like isolation in combination with ground water withdrawal systems, are preferred. Such a system consists in principle of three integrated sub systems as indicated in figure 2:

- ground water withdrawal system
- water purification
- infiltration

Depending on the quality of the purified water, infiltration can take place to rinse out the contaminants. It is also possible to drain the treated water to the surface water or to the sewer. The advantage of infiltration are the reduction of the sewage costs and a limited decrease of the ground water level.

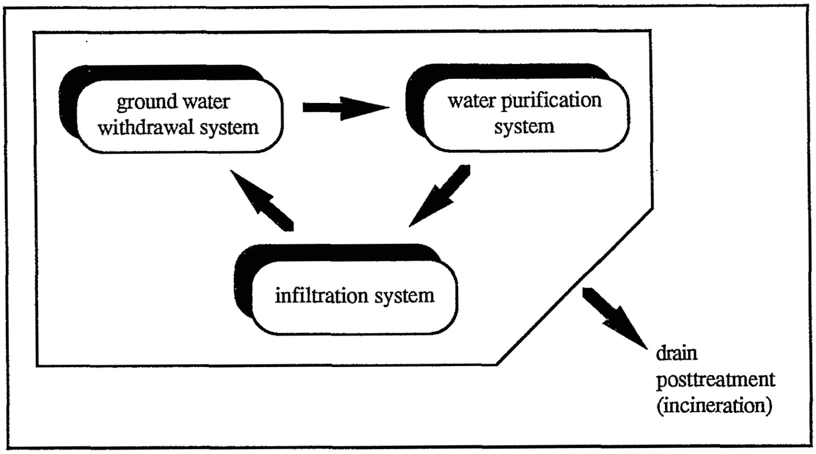


Figure 2: *Schematical representation of a ground water sanitation system*

In addition to contaminated ground water, several other aqueous waste streams can be distinguished in soil sanitation as has been shown in previous sections. In situ thermal treatment of the contaminated site requires steam to evaporate the pollutants. The steam and pollutants are collected at the surface, where they are condensed and aftertreated by means of a suitable technique. In the extraction process a lot of extraction fluids are consumed, which have to be properly purified before drainage.

Besides the sanitation of ground water, possibly in combination with soil sanitation processes and the treatment of process water in soil sanitation, water purification processes are also of importance in the treatment of percolation water from (temporary) domestic land fills and industrial waste water. For an effective purification of the contaminated water, the application of one technique is seldom very effective, because of the large differences in composition and concentration of the waste streams. This means that a combination of techniques (hybrid processes) will provide a more effective system. In table 3 a survey is presented of the conventional techniques and their applications in the treatment of contaminated water [7]. In this table the only membrane process mentioned is reverse osmosis. In a forthcoming section the role of other membrane processes in water treatment systems will be discussed.

Table 3: Survey of the available water purification techniques and their applicability [7]

Chemical classification	Biological treatment	Activated carbon adsorption	Chemical precipitation	Chemical oxidation	Chemical reduction	Ion exchange	Reverse Osmosis	Air stripping
1. Alcoholes	+++	D		+++	-		D	
2. Alifatics	D	D		0	-		D	
3. Amines	D	D		-	-			
4. Aromatics	D	+++	+	+	-		D	
5. Ethers	++	D			-			
6. Cyclic hydrocarbons halogenated alifatics	0	+++		+	-			++
7. Metals	+0	0	+++		+++	+++	+++	-
8. Miscellaneous								
Ammonia	++	-	-		-	++		++
Cyanide	++	-	-	+++	-			-
TDS	-	-	-	-	-	+++	+++	-
9. PCB's	-	+++			-			
10. Pesticides	0	+++		+++	-		+++	
11. Phenols	++	+++		+++	-		D	
12. Phtalics	++	+++	++		-			
13. Polycyclic aromatics	0+	++		++	-			

Symbols refer to the applicability: +++ very well; ++ good; + fair; 0 poor; - not; D doubtful
Insufficient results are available to give a firm based statement on the applicability in the other cases

The volatile organic hydrocarbons are an important source of pollution; they can be divided in two main categories, the aromatic hydrocarbons like benzene, toluene, styrene and xylene and the halogenated hydrocarbons like chloroform, dichloromethane and trichloroethylene. Especially the chlorinated hydrocarbons are a continuous threat to the public health [10]. Several substances of this class appear either on the so-called 'black list' or on the 'high-priority list'. Often traditional purification techniques cannot be applied to remove these components from aqueous solutions. Two techniques are applied on a technical scale [11]:

- adsorption onto activated carbon
- air stripping.

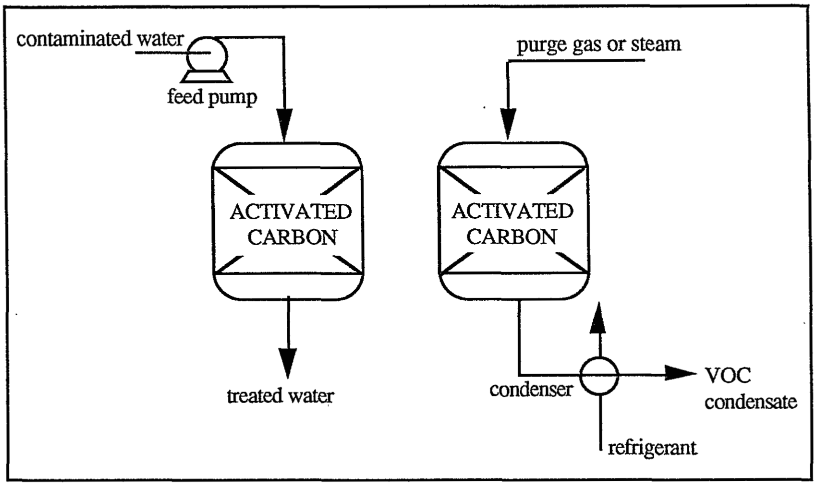


Figure 3: Schematical representation of the carbon adsorption process

Adsorption onto activated carbon is based on the physico-chemical interaction of the component to be removed and the surface of the carbon particles. Because of the extremely high specific surface area of the activated carbon a high loading capacity is obtained. After the complete internal surface is occupied, the carbon has to be regenerated. The cost of the regeneration procedure can be very high, depending on the kind of pollutant, the adsorption system and the regeneration technique.

It is also possible to use a less expensive nonregenerable kind of activated carbon. Especially in cases where regeneration is a problem, because of the large number of adsorbed substances, the use of less expensive carbon types seems to be a profitable option. The loaded carbon is incinerated or brought, often at high cost, to a landfill. In figure 3 a schematic representation is given of the activated carbon adsorption process.

Air stripping can also be applied to remove volatile organic components from aqueous solutions. Air or steam is brought in contact with the contaminated water to remove the volatile pollutant. To prevent a water pollution problem to be transferred to an air pollution problem the off-gases have to be post-treated. Several options are available to treat the stripped gases, of which gas phase adsorption onto activated carbon and biofiltration seem to be the most promising [12, 13]. In figures 4 and 5 the two possible process configurations are schematically represented.

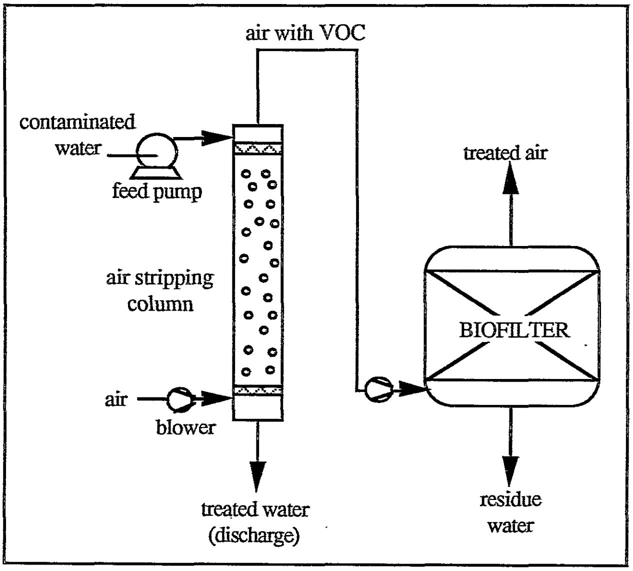


Figure 4: Schematical representation of the air stripping process in combination with biofiltration

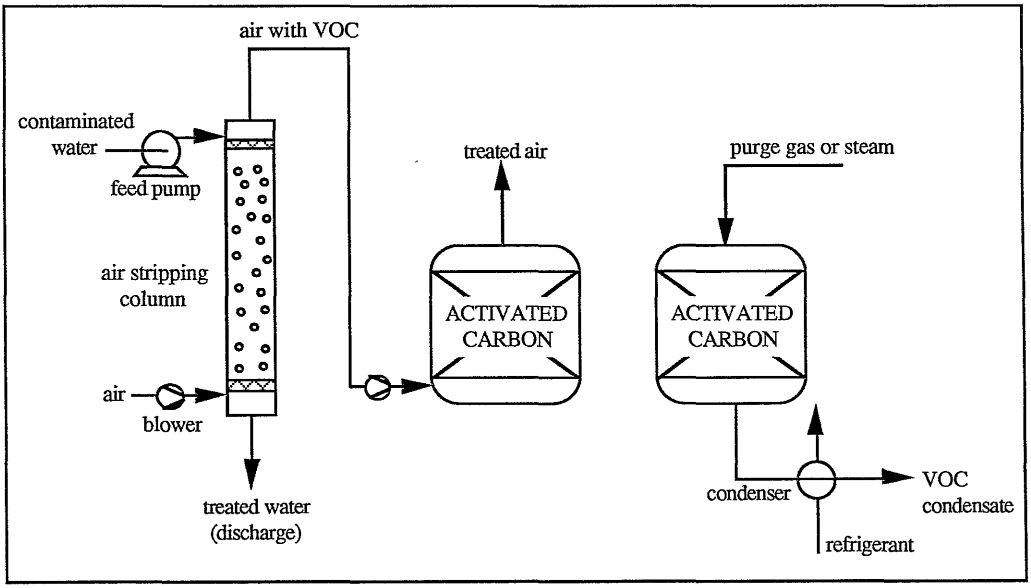


Figure 5: Schematical representation of the air stripping process in combination with activated carbon adsorption

Membrane filtration techniques provide useful alternatives for solving environmental problems. In general they possess the following specific advantages over conventional separation technologies:

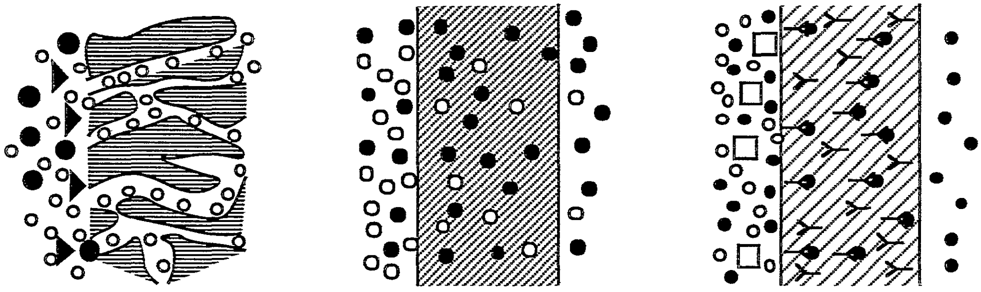
- continuous operation
- low energy consumption
- no addition of chemicals
- integration in existing industrial processes possible

The disadvantages are the possibly limited lifetime of the membranes and membrane fouling. Especially this last aspect is of great importance with respect to the application of microfiltration and ultrafiltration in environmental problems. Until now membrane processes have been applied to a limited extent in this field, although interesting applications are possible, which will be shown in the next section.

1.4 MEMBRANE PROCESSES

1.4.1 Basic aspects

A semipermeable membrane is the central part in all membrane processes. The membrane acts as a permselective barrier, through which some components can pass more readily than others. Transport takes place as a result of an applied driving force that can be provided by either a pressure, a concentration, a temperature or an electrical potential difference. The separating ability of the membranes is determined both by membrane structure and membrane material. In figure 6, different separation mechanisms are given, based on three different types of structures.



First generation
Porous
Microfiltration/Ultrafiltration
(Sieving)

Second generation
Non-porous
Pervaporation/Gas separation
(Solution-diffusion)

Third generation
Liquid
(Carrier-transport)

Figure 6: *Separation principle and membrane structure for three generations of membranes*

The first generation of membranes, which are also the most commonly known, contain pores (channels), which determine whether a substance can pass the membrane or not. It is not the type of the membrane material that determines the separation, but rather the pore size in relation with the particle size. Still the membrane material plays an important role with respect to membrane fouling and membrane cleaning. The chemical and thermal stability of the polymeric membrane is therefore important. Porous membranes are applied in micro- and ultrafiltration processes to separate large particles like bacteria and proteins from solvents like water. These porous membranes are available in a large variety of materials and configurations and from numerous suppliers.

At the moment we are at the transition from first generation membranes to second generation membranes. These second generation membranes do not contain any 'visible' pores, but have dense structures; they are used for the separation of molecules with similar sizes. These molecules can either be permanent gases, like nitrogen or oxygen (gas separation), or liquids, like ethanol and water (pervaporation). The separation is established on the basis of differences in affinity between membrane material and the separated substances as well as by differences in transport rates through the membrane. Gas separation is used commercially to separate hydrogen from other gases and pervaporation is applied in the dewatering of organic liquids. However, both processes are still in their developing stage for other separations.

The third generation are the membranes of the next century, the liquid membranes. The membrane is no longer a solid material, but a liquid. This liquid which may contain a carrier, is present in a solid porous material. The porous microfiltration membrane is just a support for the liquid, whereas the carrier molecules are responsible for the actual separation. Depending on the specificity of the carrier molecule extremely high selectivities can be established. These types of membranes show already a strong similarity with biological cell membranes.

In table 4 the characteristic features of the different membrane processes have been summarized. With respect to environmental problems several membrane processes offer interesting possibilities as indicated by several authors [14-18]. If we take a closer look at the possibilities for the use of the three generations of membranes with respect to environmental problems, specific differences can be distinguished. Microfiltration, ultrafiltration and hyperfiltration (reverse osmosis) are in principle identical processes using a hydrostatic pressure difference as the driving force for transport through the membrane. With these types of membranes the pollutant is retained, whereas the solvent passes the membrane. This accounts for microfiltration (precipitated heavy metals), as well as for ultrafiltration (oil/water emulsions) and hyperfiltration (nitrates, heavy metals and cyanides). Concentration of the pollutants can be continued until 20-30% solid content and a second purification step is required to concentrate the solution further.

Different circumstances are created using second and third generation membranes. The pollutants are not concentrated here, but selectively removed. This concept has to be preferred, because pollutants are always present in rather small amounts and the permeation of these small quantities is advantageous compared to the permeation of the large amount of bulk fluid. Gas separation systems could be a useful option for removing acid components (CO_2 and H_2S) from natural gas, the removal of SO_2 from off-gases and the separation/recovery of organic vapors from air.

Table 4: Characteristics of different membrane processes

Membrane process	**Phases* (feed/permeate)**	**Driving force**	**Separating mechanism**	**Environmental applications**
Microfiltration (industrial scale)	L+S/L G+S/G	pressure (0.1-500 kPa)	difference in size	precipitated metals oil/water emulsions
Ultrafiltration (industrial scale)	L/L	pressure (0.1-1 MPa)	difference in size	oil/water emulsions
Reverse Osmosis (industrial scale)	L/L	pressure (1-10 MPa)	solution/ diffusion	ions, heavy metals, salts nitrates from groundwater percolation water
Electrodialysis (pilot plant)	L/L	electric potential	difference in charge	ions from water
Gas separation (industrial scale)	G/G	pressure (0.1-10 MPa)	solution/ diffusion	SO_2 from off-gases vapors from air acid comp. from natural gas
Pervaporation (pilot plant)	L/G	activity	solution/ diffusion	volatile organic components from water
Membrane distillation (pilot plant)	L/G L/L	temperature	partial vapor pressure	ions from water
Pertraction (laboratory)	L/L	concentration	solubility	metals from water
Liquid membranes (laboratory)	L/L G/L G/G L/G	chemical potential difference	solubility	metal ions from water acid gases from air

* L = liquid, G = gaseous, S = solid

Third generation membranes have also good prospects in solving environmental problems. Possible applications are the removal of heavy metal ions, like mercury, cadmium and lead as well as other ions like cyanides and nitrates from ground water. It seems also possible to use liquid membranes for the selective removal of toxic gases (CO, H_2S, SO_2 and NO_x) from air. Several of these membrane processes are already applied on an industrial scale and some of them even in environmental processes as is shown in table 4.

Electrodialysis is a membrane process in which ions are removed from an aqueous solution. In this process, which is competitive with hyperfiltration, an electrical potential difference is the driving force over the ionic membrane.

Membrane distillation is a process that is not applied on a technical scale yet. Distillation takes place over the non wetted porous membrane with a temperature difference as the driving force. The membrane itself does not participate in the actual separation, but fixes the vapour phase between two liquid phases. Membrane distillation can just like hyperfiltration and electrodialysis be applied to concentrate salts from water. The process has been developed to a pilot-plant scale and commercialization can be expected within a few years time.

In pertraction, a combination of permeation and extraction, the membrane just acts as a porous inert separating barrier between a solution or a gas mixture and an extraction liquid, but there are also applications in which permselective membranes are applied. In this last case the component permeates selectively through the membrane after which the extraction fluid further increases the selectivity.

1.4.2 Some actual applications

Ground water sanitation by microfiltration [16]

A former zinc finishing factory had legally dumped acid etching baths after neutralization into the soil. At a depth of 5 meters zinc concentrations of 72 mg/l have been determined in the ground water. The total amount of dissolved zinc was estimated to be 6,000 kg. In the first instance it was decided to treat 15 m^3/h of contaminated water by an alkaline precipitation process combined with microfiltration.

The membranes applied in the microfiltration units were of the composite type and consisted of an extremely thin polymeric layer (10-50 Å) on a ceramic support. The membranes were very susceptible to fouling and a large flux decline was observed. At first these fouling problems were solved through a mechanical cleaning procedure. This, however, turned out to be insufficient, hence more powerful chemical cleaning techniques were applied. Because of these fouling problems, the fluxes were not as high as expected. Probably the polymer toplayer was destroyed during the chemical cleaning procedures, thus increasing the adsorption on the ceramic support and plugging of pores.

Soil and ground water sanitation by reverse osmosis [16]

One of the most contaminated locations in the Netherlands (Volgermeerpolder) has been selected to determine the technical applicability of a reverse osmosis process in the treatment of ground water severely contaminated with a wide range of toxic substances. Both batch and continuous experiments have been carried out. The two-stage processes was able to treat 100 l/h and consisted of two reverse osmosis units. The permeate produced in stage 1 was fed to stage 2 to obtain purified water with concentrations of the pollutants below the allowable standards for drainage. The results were encouraging, because very low final effluent concentrations have been established.

Reverse osmosis in the treatment of percolation water from domestic landfills [19, 20]

Domestic landfills can be a serious threat for the surroundings, because in the past chemical wastes, like heavy metals and halogenated hydrocarbons, have been dumped. First the landfill is isolated to prevent water flowing to the surroundings. The percolation water, heavily contaminated, cannot be drained directly to the sewage system. Membrane filtration is applied to keep the contaminants within the isolated system [19, 20]. The treatment of the percolation water by a hyperfiltration (reverse osmosis) process is schematically represented in figure 7. The percolation water is collected in a reservoir and then fed to a hyperfiltration installation. The concentrate containing the larger part of the toxic substances is reconducted to the landfill. Depending on the quality and the standard for drainage the permeate can either be further treated in a second step or directly be drained. This process is now applied on a commercial scale in which the Dutch company Stork-Friesland (The Netherlands) has supplied the membrane installations summarized in table 5 [19]. The concentrations in the contaminated water have been reduced to a level that makes it possible to drain the purified water to the sewer. Problems occurred, however, because of bacterial growth in the process water and membrane fouling through scaling effects.

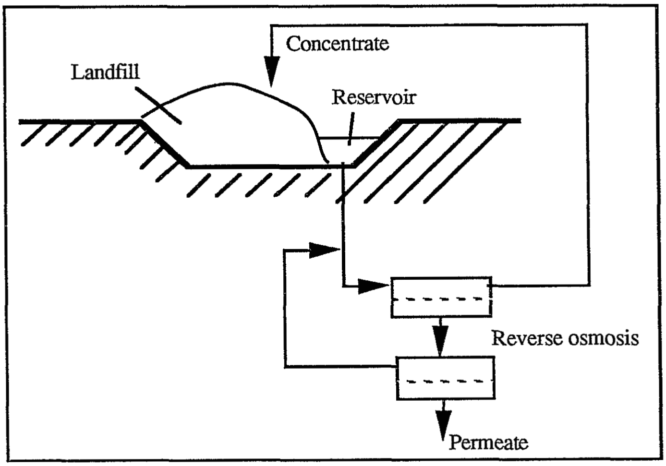


Figure 7: Treatment scheme of percolation water via reverse osmosis

Table 5: Commercial hyperfiltration installations for the treatment of percolation water

YEAR	LOCATION	CAPACITY [m^3/h]	MEMBRANE AREA [m^2]	SYSTEM
1984	Uttigen (Switzerland)	2	100	1 stage
1985	Bavel (NL)	1	100	1 stage
1986	Karlsruhe (BRD)	8	600	1 stage
1986	Wijster (NL)	23	1,500	2 stage
1987	Wieringermeer (NL)	6	600	2 stage

Vapor recovery from air [21]

GKSS (Germany) has installed a plant for the recovery of organic vapors from fuel storage tanks. The vapors produced during filling or aeration of the tanks are collected and conducted to a membrane module as schematically represented in figure 8. The permeate from the first membrane module is condensed and treated afterwards in a smaller second membrane module to further remove the remaining organics. The installation is capable of treating 300 m^3 of contaminated air per hour. The average concentration of organics is about 37 vol% and consists mainly of butane (25 %) and pentane (6.3 %). The concentration in the effluent stream just before the catalyzed incineration is 5 g/m^3, which is high enough to keep the operating temperature of the catalyst at 200 to 250 °C. Assuming the value of the recovered vapors to be Dfl 1.-/kg, the installation will have a payback time of 3 years.

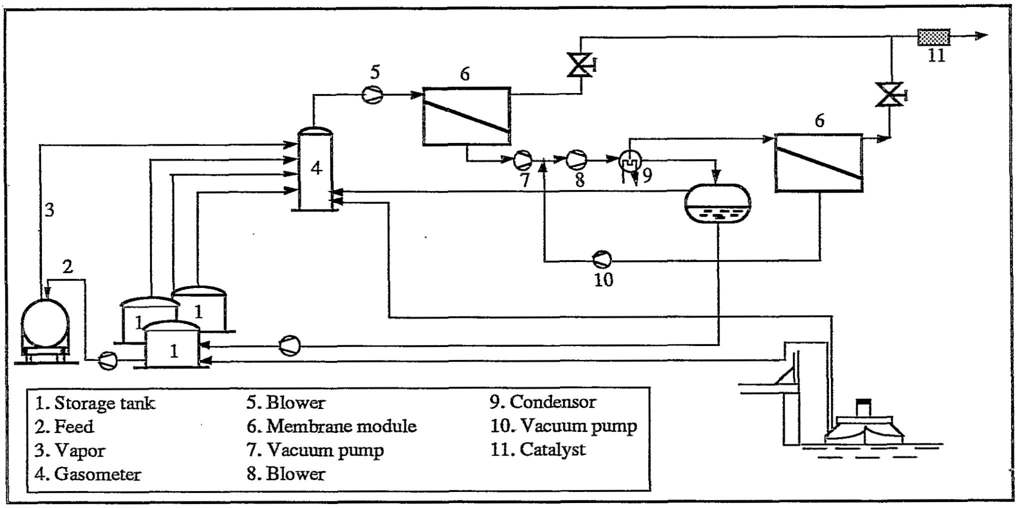


Figure 8: Installation for the recovery of vapors from air [21]

Removal of volatile organics by pervaporation [22-28]

Several authors have shown that rubber-like polymers possess the favorable selective properties for the removal of volatile organic components from water. On a pilot plant scale, experiments have been carried out by an American company MTR (Membrane Technology and Research) [22, 23] using composite silicone membranes, which are also applied in vapor recovery. It was shown that pervaporation may have good prospects in the environmental field, both with respect to economic and with respect to technical considerations. Schröder [27, 28] showed that a hybrid process of pervaporation combined with activated carbon adsorption could operate in a more cost effective way than activated carbon adsorption alone. The effluent concentration is strongly reduced in comparison with either one of the stand alone operations.

Referring now to the beginning of this chapter, it will be obvious that the question has been put in a too broad perspective. Membranes are of course not the cure for all environmental diseases, but they have the ability to solve a lot of environmental problems. With respect to the removal of volatile organic components from water pervaporation offers good prospects. The principles of this process are briefly summarized in the next section.

1.5 PERVAPORATION

Pervaporation is a membrane process, in which a liquid mixture is brought in contact with a membrane at the upstream side and the permeate is removed as a vapor at the permeate side. This is established by reducing the relative vapor pressure at the downstream side by either the use of an inert carrier gas or an applied vacuum. The vapor is obtained as a liquid in the condenser. A schematic representation of the process is given in figure 9.

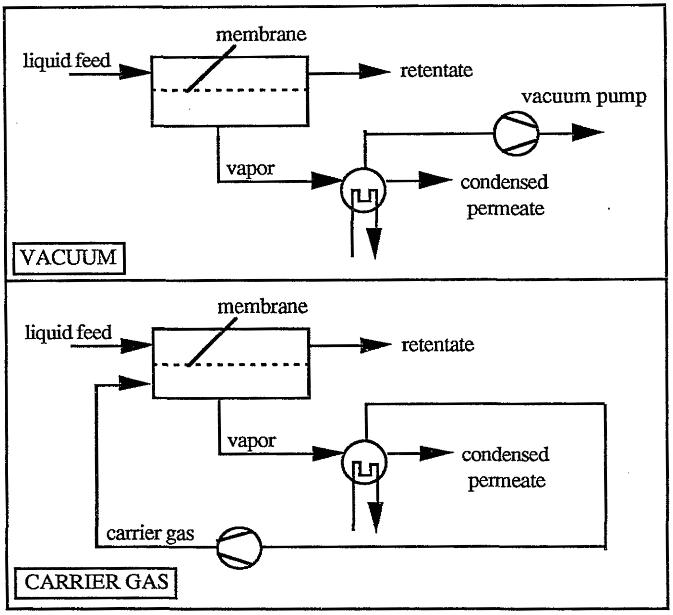


Figure 9: Schematical representation of pervaporation processes

In pervaporation a phase transition takes place, the feed is a liquid, whereas the permeate is a vapor. This implies that at least the heat of evaporation has to be supplied. Pervaporation is especially suitable for removing very small quantities from a bulk liquid. In this case only the heat of evaporation for the small amount of liquid separated has to be supplied. Furthermore, fluxes in pervaporation are relatively small, which makes the process get more profitable when only a small amount has to be removed instead of the complete bulk liquid. Important condition is, however, that the membrane has to be very selective towards the component to be removed. With respect to environmental problems this process can be applied to remove volatile organic components, like halogenated hydrocarbons and aromatics from ground or surface water.

In the pervaporation process three steps can be distinguished in the membrane:

- selective uptake of one of the components from the feed solution
- selective transport (diffusion) through the membrane
- desorption (evaporation) at the permeate side.

The first two steps are the most important and determine the transport rates observed in the membrane. The term permeability coefficient ($\mathcal{P}$) is introduced to obtain a direct relation between the observed component fluxes (J_i) in the pervaporation process, the thickness of the membrane (ℓ) and the concentration difference over the membrane (ΔC).

$$J = \mathcal{P} \cdot \frac{\Delta C}{\ell}$$

I3.1

According to the solution-diffusion model this permeability coefficient is the product of the diffusion coefficient in the membrane ($\mathcal{D}$) and the partition coefficient ($S_{M/L}$). The latter expressing the selective uptake in the polymer membrane from the liquid phase.

$$\mathcal{P} = \mathcal{D} * S_{M/L}$$

This lumped parameter ($\mathcal{P}$) is often advantageous when modelling the diffusion behaviour. With respect to this parameter two models are commonly used. Fick's law of diffusion, being the more fundamental one, makes use of diffusion coefficients, whereas the second one involves a mass transfer coefficient, a proportionality constant between the observed transport rate and the overall applied driving force.

Choosing Fick's law one is led to descriptions common to physics, physical chemistry, and biology. The original diffusion law of Fick is given as:

$$J = \mathcal{D} * \frac{dC}{dx}$$

where c means concentration of the diffusing solute. As can be seen the flux of a component is directly proportional to its concentration gradient. Modifications of this law have been proposed later on and concern the use of a fundamentally more correct chemical potential gradient, which is replaced by an activity gradient in pervaporation.

When choosing mass transfer coefficients correlations are developed used explicitly in chemical engineering. In this case the flux is described in the following way:

$$J = k * \Delta C$$

For transport in the membrane this equation can be rewritten as follows:

$$J = k_M * \Delta C = \frac{\mathcal{P}}{\ell} * \Delta C$$

The choice between these two models is a compromise between obtaining results in a very convenient way or obtaining results in a more elaborate way, but of more fundamental value. The diffusion model is the more fundamental one and is appropriate when concentrations are measured or needed versus position and time. The mass transfer model is simpler and more approximate and is especially useful when only average concentrations are involved. It also gives much easier insight in situations where transport limitations are operative outside the actual membrane (concentration polarization effects).

1.6 STRUCTURE OF THIS THESIS

The main objectives of the investigations described in this thesis are:

- the development of highly selective pervaporation membranes for the removal of

volatile organic components from water.
- description of the transport behaviour.
- the evaluation of the process economics in comparison with alternative processes.

The reader, who is merely interested in the commercial-economical aspects of removing trace organics from waste water is referred to chapter 6. For the reader with an interest in mass transfer limitations chapters 2 and 3 are the most interesting ones, whereas more fundamental aspects on membrane performance are given in chapters 4 and 5.

When it was decided from a literature study, that elastomeric membranes would probably have the best potential in this field, the pervaporation behaviour of several (thick) elastomeric membranes has been studied. On the basis of these results and those obtained with a semi-technical pervaporation installation the economics of the process have been evaluated. The necessity to improve the pervaporation performance of the relatively thick homogeneous membranes was evident. Two possible ways in which this can be established, viz. the reduction of the effective membrane thickness and the improvement of the mass transport at the feed side of the membrane, have successively been investigated. Additionally a more fundamental aspect of the membrane itself, the preferential sorption of the liquid feed components in the membrane, has been studied. All these different aspects can be found back in the various chapters of this thesis.

In chapter 2 a resistance-in-series model is presented, which can describe the pervaporation performance of elastomeric membranes in the removal of trace organics from water. The model is verified using both composite and homogeneous membranes with a wide range of thicknesses. Transport in the stagnant liquid boundary layer seems to be of predominant importance in the pervaporation performance.

In chapter 3 the transport of the organic component in the liquid boundary layer at the membrane interface has been studied. Using the model presented in chapter 2 boundary layer mass transfer coefficients have been obtained from experiments with different pervaporation cells and membranes. Theoretical mass transfer coefficients can be obtained with reasonable accuracy from mass transfer correlations.

In chapter 4 the pervaporation behaviour of various homogeneous elastomeric membranes in the removal of volatile organic components from aqueous solutions has been described. True membrane permeability data have been derived using the equations explored in the previous chapters. The permeability data are qualitatively explained in terms of the solution-diffusion model, whereas more quantitatively the data are related to solubility parameters and glass transition temperatures. Large differences in selectivities have been observed, which can be attributed almost completely to differences in the water transport through these membranes.

In chapter 5 the sorption behaviour of elastomeric membranes in dilute aqueous solutions of organics has been investigated. Flory-Huggins thermodynamics can be applied to predict the sorption behaviour of the polymeric films.

In chapter 6 the pervaporation process has been evaluated both with respect to economic as well as to technical considerations and has been compared with alternative processes. Pervaporation is a generally applicable and economically attractive process for the treatment of aqueous waste streams contaminated with moderate and high concentrations of volatile organic components.

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CHAPTER 2

RESISTANCES IN SERIES: EFFECT OF MEMBRANE THICKNESS

H.H. Nijhuis, M.H.V. Mulder and C.A. Smolders

SUMMARY

A resistance-in-series model is used to describe the pervaporation performance of elastomeric membranes in the removal of volatile organic components from water. Equations are derived to describe the organic component flux as a function of feed concentration, Henry-type of partition coefficient, diffusion coefficient in the membrane, membrane thickness and boundary layer mass transfer coefficient. The model has been verified using both homogeneous and composite membranes of polydimethylsiloxane, ethylene propylene rubber and polyoctenamer. Membranes with a wide range of thicknesses have been prepared and the pervaporation behaviour for the removal of toluene and trichloroethylene from aqueous solutions has been studied. Mass transfer coefficients in the liquid boundary layer and in the membrane respectively have been determined. The experiments show that the hydrodynamic boundary layer resistance is of great importance. For highly permeable polymers such as polydimethylsiloxane mass transfer in the boundary layer is rate determining and should be considered carefully in further development of this process. For less permeable polymers such as ethylene propylene rubber this effect becomes more dominant with decreasing membrane thickness.

The water fluxes are inversely proportional to the thickness of the actual separating layer and they depend strongly on the type of elastomer used. A proper choice of the elastomeric material and the thickness of the separating layer will determine the selectivity of the process.

2.1 INTRODUCTION

All over the world including the Netherlands a large number of locations are known where the soil is severely contaminated. Today a number of different techniques are available that can be used to reduce or solve this problem. These techniques can roughly be divided into four categories:

- thermal techniques;
- biological treatment;

- extraction;
- isolation.

The last technique is not a cleaning technique in itself, but prevents further emission to the surroundings. In cases where the pollutant has little or no interaction with the soil particles a combination of isolation, ground water withdrawal, water purification techniques and -if possible- infiltration of the purified water is a feasible procedure to clean the soil, as schematically represented in figure 1. The advantages of this procedure are the low initial costs, the simplicity, the avoidance of soil excavation and the additional sanitation of the groundwater. A clear disadvantage is the long soil cleaning time (10 - 25 years) inherent to this method [1]. Because in most cases the time for treatment of the soil is limited, alternative techniques are preferred.

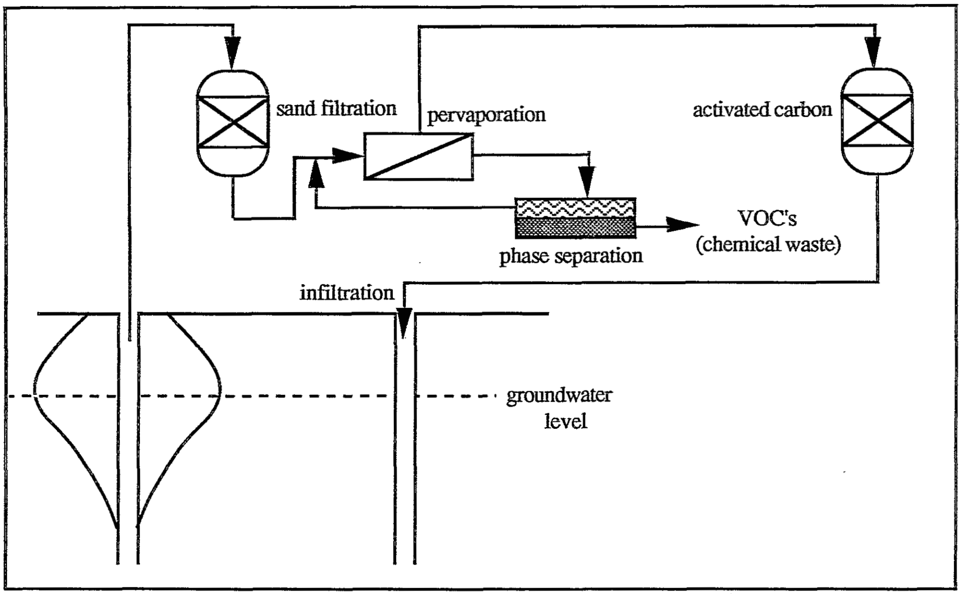


Figure 1: Ground water withdrawal in combination with pervaporation and activated carbon adsorption to remove volatile organic components

Membrane filtration offers good prospects to solve environmental problems. Until now only traditional membrane filtration techniques like micro-, ultra- and hyperfiltration are being used. These pressure driven processes have the disadvantage that the polluting compounds are concentrated and not selectively removed from the feed solution. For environmental applications where often very small quantities of toxic substances are present, techniques should be preferred, which remove selectively the polluting compounds.

With respect to this, pervaporation offers good prospects in the removal of trace organics from aqueous solutions. The attractiveness of pervaporation, in contrast to existing techniques, lies in the fact that the pollutant is selectively removed from the feed as an almost pure liquid. In a previous study [2] extremely high selectivities are reported for relatively thick dense homogeneous elastomeric membranes. A decrease in membrane thickness should further improve the already reasonable fluxes.

Several authors pointed at the important role of a hydrodynamic boundary layer resistance at the feed side of the membrane [3, 4], causing a strong decrease in pervaporation selectivity using thinner membranes. This phenomenon observed at the membrane interface is referred to as concentration polarization. In contrast to large effects found for pressure driven membrane filtration techniques it was generally assumed that for gas separation and pervaporation concentration polarization was of minor importance, because of the low transport rates observed in these processes combined with a relatively high mass transfer coefficient in the feed mixture. Only recently, however, data were published from which it is evident that the phenomenon of concentration polarization can not be neglected a priori [5-10].

In this chapter a resistance-in-series model will be discussed, similar to the work of Côté and Lipski [4]. The effect of membrane thickness on the performance of pervaporation membranes in the removal of volatile organic components from aqueous solutions will be described and mass transfer coefficients for the boundary layer and the membrane respectively will be determined.

2.2 THEORY

2.2.1 General

Figure 2 gives a schematic representation of the concentration profile of the preferentially permeating component in the pervaporation process. Three different volume flows can be distinguished:

1) Convective flow of the components towards the membrane denoted by J^c.

This flow is a result of the transport of components from the feed towards the membrane.

2) Diffusional flow of the components in the boundary layer, denoted by J^d.
   This flow is due to the concentration gradients of the components in the boundary layer.
3) Permeation of the components through the membrane, denoted by J^p.
   This flow is due to the concentration gradient of the components inside the membrane.

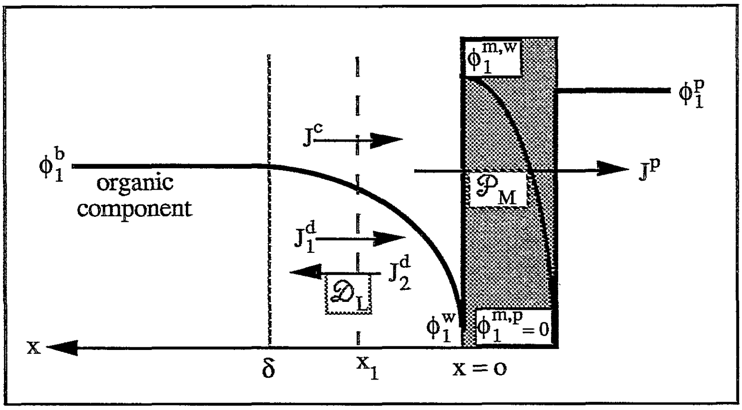


Figure 2: Concentration profile of the organic component in the boundary layer and in the membrane (ϕ means volume fraction)

In the stationary state the volume and the mass of a volume element, between $x = 0$ and $x = x_1$, must be constant. The volume balances over this volume element are:

Total: $$J^c - J^d - J^p = 0 \qquad (1)$$

Component i: $$J_i^c - J_i^d - J_i^p = 0 \qquad (i = 1, 2) \qquad (2)$$

J_i^c, J_i^d and J_i^p are the component volume flows due to convection, diffusion and permeation, respectively. The different flows of component 1 can be calculated as follows:

convection: $$J_1^c = J^c \, . \, \phi_1 \, (x) \qquad (3)$$

permeation: $$J_1^p = J^p \cdot \phi_1^p \tag{4}$$

The component flows due to diffusion are described by Fick's Law:

$$J_1^d = - \mathcal{D}_1 \frac{d\,\phi_1(x)}{d\,x} \tag{5a}$$

$$J_2^d = - \mathcal{D}_2 \frac{d\,\phi_2(x)}{d\,x} \tag{5b}$$

In the equations given above $\phi_1(x)$ and $\phi_2(x)$ represent the volume fraction of component 1 and 2 respectively at a distance x from the membrane wall and ϕ_1^p the volume fraction of component 1 in the condensed permeate.

The well known film theory relationship [11] for the preferentially permeating component 1 given below can now be derived, taking into account that in a binary liquid mixture only one diffusion coefficient, the mutual diffusion coefficient ($\mathcal{D}_L$), exists ($\mathcal{D}_L = \mathcal{D}_1 = \mathcal{D}_2$).

$$J^p = \frac{\mathcal{D}_L}{\delta} \ln\left(\frac{\phi_1^w - \phi_1^p}{\phi_1^b - \phi_1^p}\right) \tag{6}$$

In equation (6) the total permeate flow J^p is given as a function of the diffusion coefficient of the organic component in the aqueous solution ($\mathcal{D}_L$), the thickness of the liquid boundary layer (δ) and the volume fraction of the preferentially permeating component 1 at the membrane interface, in the permeate and in the bulk feed solution.

2.2.2 Boundary layer resistance

The logarithmic function in equation (6) can be rewritten and rearranged as shown in the appendix, thus finally yielding a simple equation for the mass transfer in dilute solutions:

$$J^p.\delta = \mathcal{D}_L \frac{\phi_1^b - \phi_1^w}{\phi_1^p} \qquad (7)$$

Combination of equations (4), (7) and substitution of $\mathcal{D}_L/\delta$ by the mass transfer coefficient k_L gives:

$$J_1^p = k_L\,(\phi_1^b - \phi_1^w) \qquad (8)$$

Equation (8) has been derived using the following assumptions:

- Transport due to density or temperature gradients is neglected;
- Diffusion coefficients are constant in the boundary layer;
- Concentrations are low;
- The boundary layer mass transfer coefficient is independent of the flux and the concentration.

Equation (8) can also be derived, assuming that the convective flux is negligible as is shown by Psaume et. al. [3]. If the membrane resistance can be neglected and the membrane wall concentration is small compared to the bulk concentration an even simpler equation is derived:

$$J_1^p = k_L \, . \, \phi_1^b \qquad \text{if: } \phi_1^w \ll \phi_1^b \qquad (9)$$

2.2.3 Membrane resistance

For a large number of materials the membrane resistance can not be neglected 'a priori'. Côté and Lipski [4] showed that at high cross-flow velocities the membrane resistance may become important. The membrane wall concentration in equation (8) can no longer be assumed to be zero and a second equation has to be derived in order to calculate this concentration.

Transport in the membrane can as a first approximation be described by the volumetric form of Fick's law.

$$J_i^p = - \mathcal{D}_i^m \, . \, \frac{d\phi_i^m(x)}{dx} \qquad (10)$$

In the case of a low relative vapor pressure at the permeate side of the membrane (zero concentration) and with constant diffusion coefficients in the membrane (independent of concentration), integration of equation (10) gives:

$$J_i^p = \mathscr{D}_i^m \cdot \frac{\phi_i^{m,w}}{\ell} \qquad (11)$$

The unknown wall concentration in the membrane $\phi_1^{m,w}$ can be eliminated, if a Henry-type of partition coefficient is assumed:

$$S_{M/L} = \phi_1^{m,w} \big/ \phi_1^w \qquad (12)$$

Substitution in equation (11) gives:

$$J_1^p = \frac{\mathscr{D}_1^m \cdot S_{M/L}}{\ell} \cdot \phi_1^w = k_M \cdot \phi_1^w \qquad (13)$$

If equations (13) and (8) are rewritten as the product of flux (J) and resistance (1/k) the following equations are obtained:

$$\frac{1}{k_L} \cdot J_1^p = \phi_1^b - \phi_1^w \qquad (14)$$

$$\frac{1}{k_M} \cdot J_1^p = \phi_1^w \qquad (15)$$

Substitution of ϕ_1^w in equation (14) by equation (15) gives:

$$\left(\frac{1}{k_M} + \frac{1}{k_L}\right) \cdot J_1^p = \frac{1}{k_{OV}} \cdot J_1^p = \phi_1^b \qquad (16)$$

The overall mass transfer coefficient k_{OV}, can simply be determined from measurements of feed concentration and the steady state permeate component flux in the pervaporation experiments.

3.1

$$J_1^p = k_{OV} \cdot \phi_1^b \qquad (17)$$

The reciprocal overall mass transfer coefficient ($1/k_{OV}$) can be considered as the sum of:

- a liquid boundary layer resistance ($1/k_L$) and
- a membrane resistance ($1/k_M = \ell / (S_{M/L} \cdot \mathcal{D}_1^m)$)

According to the solution-diffusion model the product of partition coefficient and diffusivity is equal to the membrane permeability ($\mathcal{P} = \mathcal{D} \times S$). Therefore the overall membrane resistance can be written as:

$$\frac{1}{k_{OV}} = \frac{1}{k_L} + \frac{1}{k_M} = \frac{1}{k_L} + \frac{\ell}{\mathcal{P}_1^m} \qquad (18)$$

3.1

2.2.4 Influence of different parameters on the pervaporation performance

From equations (17) and (18) it can be seen that the pervaporation performance in the removal of volatile organic components from water is influenced by several parameters:

- feed concentration (ϕ_1^b);
- boundary layer mass transfer coefficient (k_L);
- membrane permeability ($\mathcal{P}_1^m$);
- membrane thickness (ℓ)

The boundary layer resistance ($1/k_L$) is strongly influenced by the flow conditions at the feed side of the membrane (Reynolds number) and the configuration of the cell, while the membrane resistance is related to parameters like membrane thickness and permeability. With increasing flow velocity the boundary layer resistance decreases and the membrane resistance ($1/k_M = \ell / \mathcal{P}_1^m$) becomes more important. Especially for relatively thick homogeneous membranes with a low permeability for the organic component, the membrane resistance, which is supposed to be directly proportional to the membrane thickness, will be rate determining. If the overall mass transfer resistance is plotted as a function of the membrane thickness a straight line is obtained for which the intercept is equal to the liquid boundary layer resistance and the slope is equal to the reciprocal value of the membrane permeability (see figure 3).

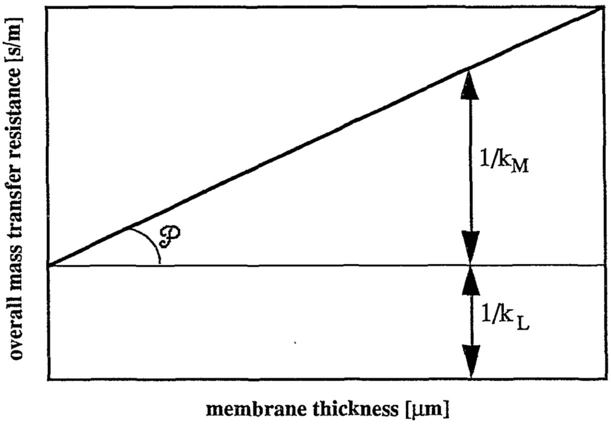


Figure 3: Mass transfer resistances as a function of membrane thickness

2.3 EXPERIMENTAL

2.3.1 Materials

Polyvinylidenefluoride (PVDF) and polysulfone (PSf) were used as materials for the support for the composite membranes. Polydimethylsiloxane (PDMS; RTV 615 A) and crosslinking agent (RTV 615 B) were purchased from General Electric and used for the preparation of dense homogeneous membranes and for the thin toplayer in composite membranes. Ethylene propylene rubber (EPDM) and polyoctenamer (OT) were kindly supplied by Helvoet BV.; Hellevoetsluis; Netherlands.

The solvents (analytical grade) for dissolving the polymers and the crosslinking agent dicumylperoxide (DCP) were obtained from Merck. The polymers and chemicals were used without further purification.

For homogenization of the demixed permeate, ethanol was used of analytical grade and dried on molecular sieves.

Water was deionized and ultrafiltrated before use.

2.3.2 Membrane preparation

Three polymer materials have been selected on the basis of a previous study [2]. Silicone rubber (PDMS), already used by several authors in the removal of volatile organic components from aqueous solutions, is selected, because of the extremely high permeation rates. Ethylene propylene rubber (EPDM) and polyoctenamer (OT) have been investigated, because they combine extremely high selectivities towards the organic component, to reasonable organic component fluxes. Both dense homogeneous and composite membranes with an elastomeric toplayer have been prepared by a standard casting procedure.

For the preparation of homogeneous EPDM and OT membranes the polymers are dissolved in a suitable solvent and a certain amount of DCP is added. The polymer solutions of EPDM are casted on a clean glass plate and the solvent is evaporated overnight. For the preparation of OT membranes Teflon® plates are used. The next day the elastomers are crosslinked during 45 minutes at 155 °C. After cooling, the plates are placed in a water bath and after 24 hours the membranes are carefully removed from the plates. The evaporation, crosslinking and cooling step are carried out in a nitrogen atmosphere. In this way membranes are obtained with thicknesses in the range of 40 - 200 μm.

For the preparation of PDMS membranes a different procedure is followed. The polymer and crosslinking agent are purchased from General Electric (RTV 615 A + B). The two components are mixed and when the solution is free of air bubbles the solution is casted on a Perspex® (polymethylmethacrylate) plate. To reduce the time of crosslinking the silicone rubber membranes are cured on the plate at 70 °C overnight in a nitrogen atmosphere. The thicknesses of the PDMS membranes thus obtained was 30 - 240 μm.

The flat composite membranes consist of three layers (see figure 4):

- non woven fabric;
- porous support of PVDF or PSf;
- dense elastomeric toplayer.

The supports of PVDF or PSF were prepared by casting of a polymer solution upon the non woven fabric followed by immersion precipitation. In this way membranes are obtained with ultrafiltration characteristics.

The dense elastomeric toplayer has been applied upon the porous support by casting of a polymeric solution and evaporation of the solvent in a nitrogen atmosphere. DCP was added to the polymeric solutions of EPDM and OT in order to crosslink the toplayers in a nitrogen atmosphere by an UV initiated crosslinking reaction at 70 °C [12, 13]. PDMS toplayers already consisted of two components (General Electric RTV 615 A+B) and are crosslinked at 70 °C in a nitrogen atmosphere.

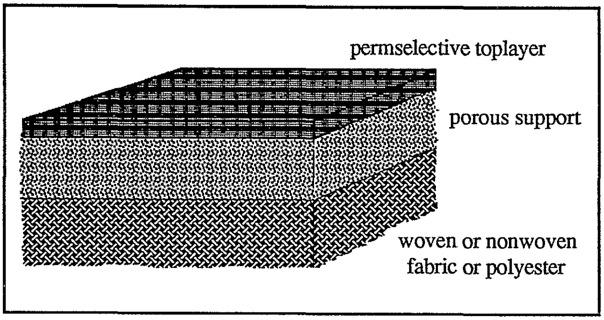


Figure 4: Schematic drawing of a composite membrane

2.3.3 Membrane characterization

The porous substructure was characterized by measurement of the pure water flux at a pressure of 3 bar with a standard laboratory ultrafiltration set-up.

The thickness of the silicone toplayers was determined by measurement of oxygen and nitrogen permeability. Provided that the gas permeability of PDMS is known, the effective membrane thickness can be calculated from this value assuming an inverse proportionality. Furthermore the membrane area should be known, whereas the pressure difference over the membrane and the gas permeate flow should be determined. A permeability ratio for oxygen/nitrogen of at least two indicates that the membrane is defect free. The permeation rates for EPDM and OT were too small to be measured in our simple gas permeation set-up and their toplayer thickness was determined in another way as will be described below. The thickness of the actual separating layer for the composite membranes ranged from 5 to 70 µm.

Scanning Electron Microscopy was used to check the effective membrane thickness determined in this way.

2.3.4 Pervaporation experiments

The pervaporation data are obtained with the set-up schematically represented in figure 5. The apparatus consists of a thermo-regulated 5 liter storage tank with Viton® feed and recycle lines. The concentration of the feed solution in the glass tank is kept constant by a continuous supply of organic component to the liquid feed. The aqueous solution, with a temperature of 25 °C is circulated through three pervaporation cells in series. A centrifugal pump allows an average flow rate in this set-up of 2 l/min, which is large enough to prevent a concentration drop over the three cells. Syringe sampling of the feed for GC analysis was done periodically through a silicone rubber septum.

The pervaporation cell, schematically represented in figure 6, consists of an upstream and a downstream half cell. The liquid feed flows through the upstream side, bringing the upper side of the membrane in contact with the liquid.

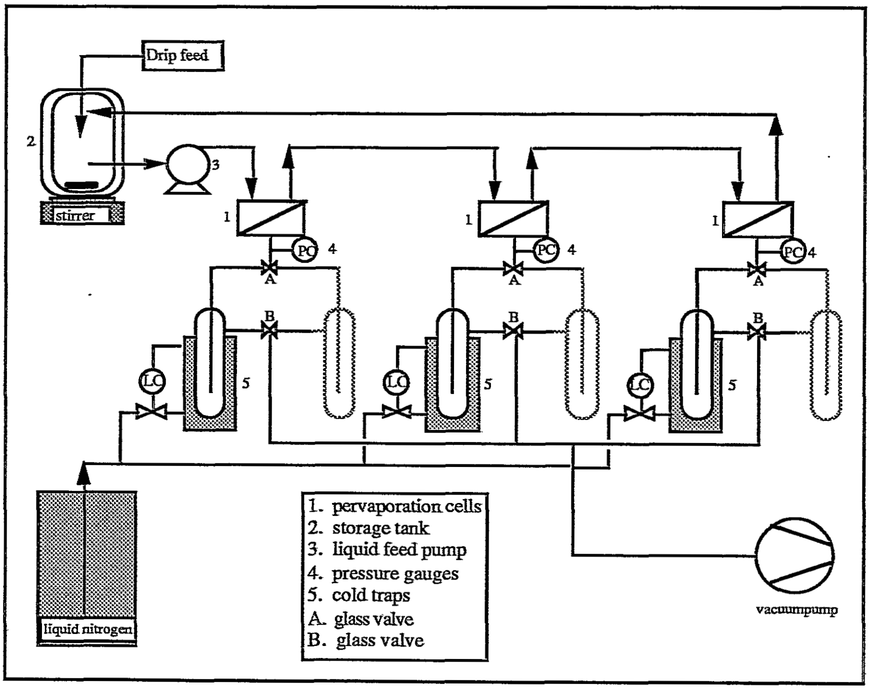
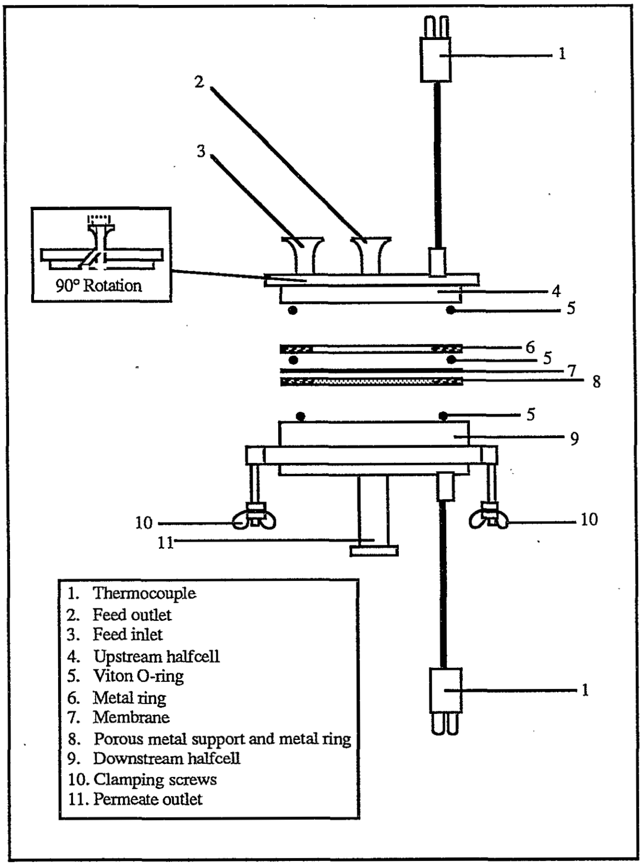


Figure 5: Schematic diagram of the experimental set-up



<u>Figure 6:</u> Schematical representation of the pervaporation cell

The permeate is collected in cold traps, cooled with liquid nitrogen (- 196 °C). The level of the liquid nitrogen in the dewars is controlled by a level control, a large storage tank (50 liter) and three low temperature resistant electrical valves. The downstream side of the set-up offers the possibility of continuous operation by turning the glass valves, indicated by A and B in figure 5. For measuring the pressure at the permeate side each cell is supplied with a pressure gauge (Edwards type PRM 10) close to the permeate side of the membrane. The pressure can be read with a pressure controller (Edwards; type 1101), which also operates as a safety device shutting the system down in case of a sudden pressure rise. The vacuum in the system is maintained by means of an Edwards two stage vacuum pump.

Steady state operating conditions were achieved after 3 - 4 days of pervaporation. After the permeate was collected, the component fluxes were determined, according to the following equation:

Component flux: $$J_i^p = \frac{m}{A\,.\,t}\,.\,\frac{w_i^p}{\rho_i} \qquad (19)$$

The concentrations of the liquid mixtures were in the range of 100 - 500 µg/g which allows to assume a concentration independent feed density of approximately 1000 kg/m^3.

2.4 RESULTS AND DISCUSSION

2.4.1 Substructure (thermal stability during crosslinking by heat)

Ultrafiltration membranes obtained by immersion precipitation have been used as support for the elastomeric toplayers. Crosslinking of the elastomers is necessary to prevent high swelling and loss of mechanical strength and consequently loss of pervaporation performance. Crosslinking times of 30 - 60 minutes are found to be necessary at temperatures of 150 °C and higher for dicumylperoxide (DCP) [14]. The thermal stability of the PVDF and PSf supports against a heat treatment for one hour at 155 °C is poor, while solvents to be used during casting had only a small influence on the characteristics of the substructure. As an example ultrafiltration pure water flux data for PVDF are given in table 1.

Table 1: Ultrafiltration pure water fluxes of the porous substructure (PVDF) under various conditions

pretreatment type	CCl_4	Hexane	155 °C	UV
	pure water flux [kg/m^2.hr]			
before pretreatment	46	38	44	41
after pretreatment	34	33	14	38

Because of the poor thermal stability of the support a different method of crosslinking was used. Dense homogeneous elastomeric films containing DCP were UV-irradiated at 70 °C in a nitrogen atmosphere. The films obtained in this way showed good mechanical strength and limited swelling even after one week of immersion in the polymer solvent. As shown in table 1 the UF pure water flux for the porous support is not altered due to this irradiation process.

Scanning Electron Microscopy showed no visible changes of the porous support due to either a heat treatment, UV-irradiation or a treatment with the elastomer solvent.

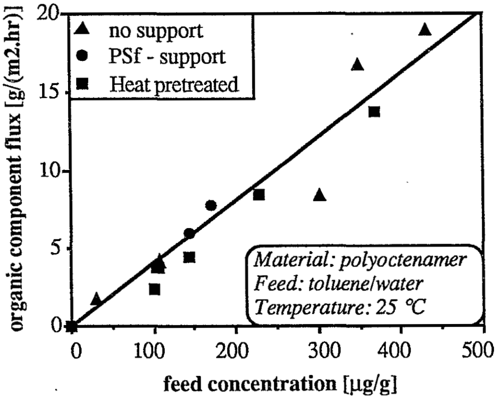


Figure 7: Influence of the porous support on pervaporation performance

After evaluating the influence of several parameters in the preparation of composite membranes on the porous support, it is also of interest to determine the influence of the support on the pervaporation performance. Figure 7 shows the flux of the organic component as a function of the feed concentration for a homogeneous OT-membrane. The same membrane is used again, now upon a porous PSf support. In a third experiment the same homogeneous membrane was installed on a PSf support that had been heat treated for one hour at 155 °C. The influence of the substructure, that had not been pretreated, seems to be negligible, at least for the relatively thick OT-membrane used for this purpose. The heat treated support showed a somewhat higher resistance against mass transfer of the organic component. The differences in organic fluxes are, however, only small, in contrast with the large drop in pure water flux of the thermally treated support, showing the minor influence of the porous support on pervaporation performance in comparison with other resistances present.

2.4.2 Toplayer thickness

The thickness of the actual separating layer of the silicone composite membranes was determined by oxygen/nitrogen permeability measurements. An alternative method for determining the toplayer thickness, however, was developed for cases of too low gas fluxes. The water fluxes, which are independent of the concentration of organics in the aqueous solution [15-17], appear to be inversely proportional to the effective thickness of the membrane as shown in figure 8. On the horizontal axis both the effective membrane thickness of composites, determined by gas permeability and the thickness of the homogeneous membranes, determined with a digital micrometer, are given. The mean pervaporation water fluxes are given on the vertical axis. For comparison the water fluxes for EPDM membranes are also given in this figure; they are roughly 100 times smaller at comparable thicknesses.

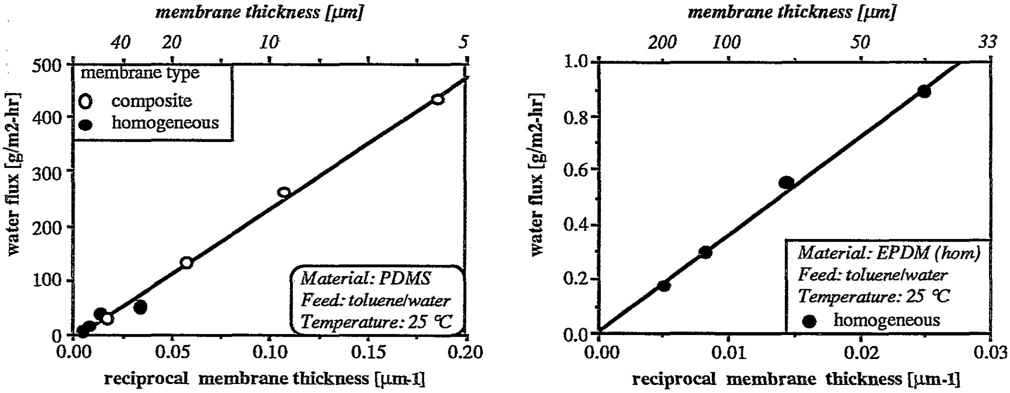


Figure 8: Water fluxes obtained from liquid feed mixtures as a function of reciprocal membrane thickness for PDMS (left) and EPDM (right) membranes.

2.4.3 Determination of the overall mass transfer coefficient

The overall mass transfer coefficient (k_{OV}) can be determined from a plot of the organic component flux (J_{OC}) over the feed concentration (ϕ_1^b). A linear regression fitting procedure is followed to obtain this k_{OV} value from the slope, while the intercept is smaller than 0.2.

In this way overall mass transfer coefficients have been determined for EPDM, OT and PDMS membranes.

Ethylene propylene rubber

Two homogeneous EPDM membranes have been prepared with thicknesses of 50 and 140 μm respectively. The pervaporation results as a function of the trichloroethylene concentration are given in figure 9. The overall mass transfer coefficients calculated from the slopes of the lines are 1.3 * 10^{-5} m/s for the thinner and 0.90 * 10^{-5} m/s for the thicker membrane. Although a higher slope for the thinner membrane is observed, the overall mass transfer coefficients differ only by a factor of 1.4, while the reciprocal ratio of the thicknesses is 2.8. This indicates that an inverse proportionality between the organic component flux and the membrane thickness could not be established, hence a liquid boundary layer resistance does exist even for these relatively thick membranes.

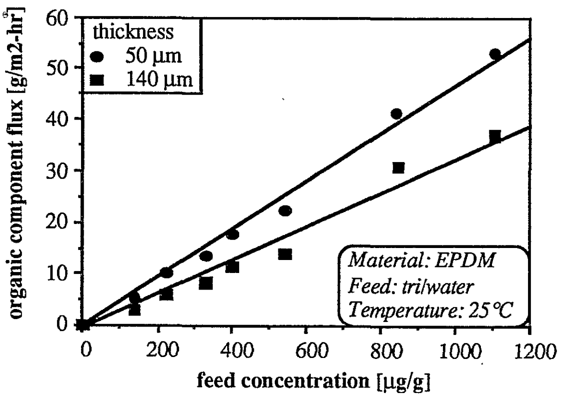


Figure 9: Trichloroethylene component fluxes for homogeneous EPDM membranes as a function of the feed concentration

The possible effect of different supports has been checked again in the following way. Thin permselective toplayers of EPDM were applied on PVDF and PSf supports to reduce the toplayer resistance to extremely low (negligible) values. The pervaporation performance was determined for an aqueous solution of toluene with a concentration of 200 μg/g. The pervaporation water fluxes indicated that very thin toplayer thicknesses had been obtained. The effective thicknesses of the investigated membranes were different, but both for the PVDF as for the PSf support less than 1 μm. This was confirmed by SEM. From the organic component fluxes (19.5 and 18.4 g/(m2.hr) respectively) the overall mass transfer coefficients were calculated as $2.7*10^{-5}$ m/s and $2.6*10^{-5}$ m/s for the two supports. From this experiment it is clear that both porous supports do not contribute to the overall mass transfer of the organic component. PSf supports already proved to have a negligible resistance, in comparison with other resistances present, and therefore experiments performed with the different supports, can be compared with each other.

Polyoctenamer

Extremely high selectivities made OT a very promising material for the extraction of volatile organic components from water. Two composite membranes have been prepared consisting of a PVDF support and an OT toplayer. The pure pervaporation water fluxes have been determined and were 23 and 1.0 g/(m^2.hr) respectively, from which toplayer thicknesses of 5 and 150 μm were calculated and confirmed by SEM-photographs.

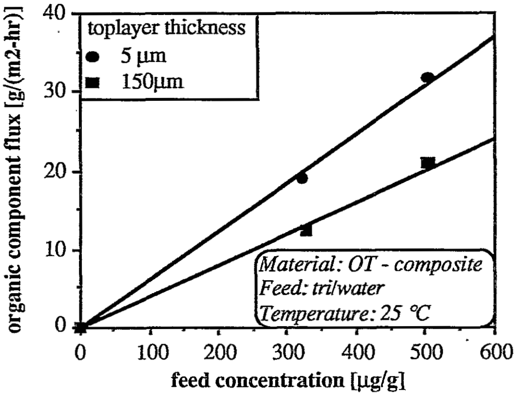


Figure 10: Trichloroethylene component fluxes for OT-composite membranes as a function of feed concentration

In figure 10 the results for the two composite membranes are summarized. From the slopes of these curves overall mass transfer coefficients can be calculated as $1.7 * 10^{-5}$ m/s and $1.1 * 10^{-5}$

m/s respectively. It is clear from these results that the membrane resistance has practically no influence even for a 30-fold reduction in toplayer thickness.

Polydimethylsiloxane

The presence of the membrane resistance shows up least of all with composite membranes consisting of a PDMS toplayer on a PSf-support. Results for aqueous solutions of trichloroethylene and toluene are summarized in figure 11. The solid lines in these figures represent the fit obtained when all experimental values are considered in a linear regression fitting procedure, irrespective of the effective membrane thickness. It is remarkable to see that for the organic component fluxes only minor deviations from the straight line are observed, although composite membranes were used with toplayers of various thicknesses. Obviously the resistance of the membrane contributes only to a minor extent to overall resistance towards mass transfer of the organic component.

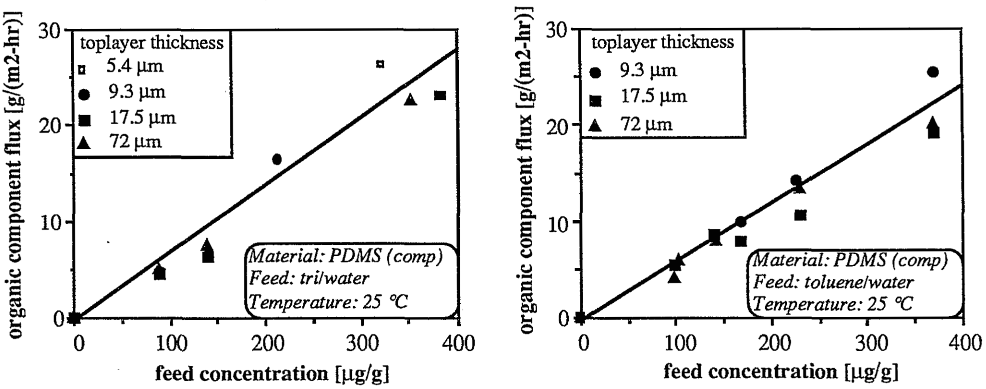


Figure 11: Trichloroethylene fluxes (left) and toluene fluxes (right) for PDMS-composite membranes as a function of the feed concentration of the organic component in water

From the experiments described above the permeability coefficients of the organic component in PDMS membranes could not be determined in a very accurate way. However, more accurate data may be obtained from experiments with dense homogeneous membranes. The thicknesses of these membranes should then vary over a wide range. This is described in the next section.

2.4.4 Determination of mass transfer resistances

The overall mass transfer coefficient (k_{OV}), can be calculated from a plot of the organic component flux vs. the concentration (see figure 9). Because straight lines are obtained, an alternative less time consuming way of determining the overall resistance ($1/k_{OV}$) has been used. The ratio of the organic component flux and its bulk concentration at one fixed composition of the feed mixture gives the desired value for the overall mass transfer coefficient. For dense homogeneous membranes of PDMS and EPDM, the boundary layer and the membrane resistance have been determined in this way from experiments with toluene as the organic component.

The component fluxes for dense homogeneous membranes of PDMS and EPDM with thicknesses in the range of 30 to 240 µm are given in figure 12. Organic component fluxes of 13 to 20 g/m^2.hr at a concentration of 250 µg/g are obtained for PDMS membranes, while the water fluxes ranged from 6 to 51 g/m^2.hr. For EPDM membranes toluene fluxes at a constant concentration of 250 µg/g could be calculated of 3.5 to 8.5 g/m^2.hr, while the water fluxes ranged from 0.17 to 0.89 g/m^2.hr.

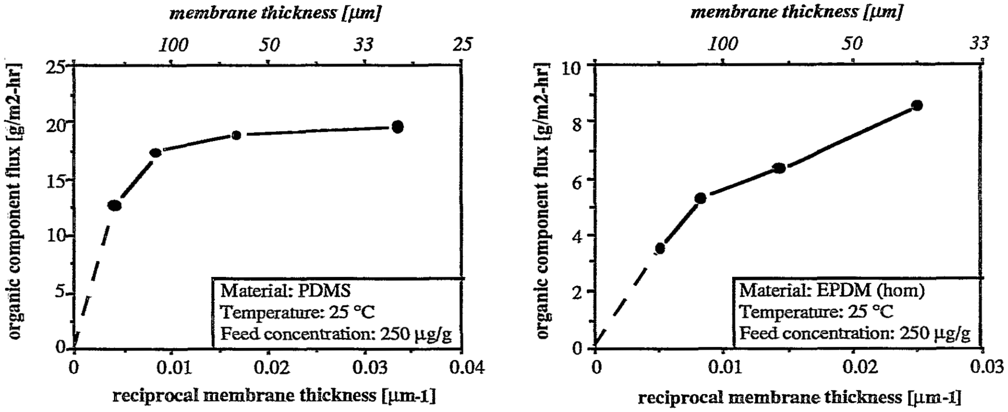
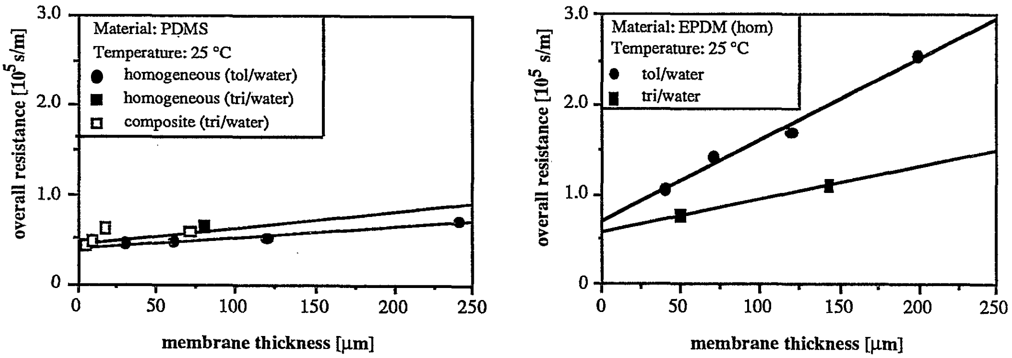


Figure 12: Organic component fluxes as a function of reciprocal membrane thickness for PDMS (left) and EPDM (right) membranes

Figure 13 gives the calculated overall resistance ($1/k_{OV}$) as a function of the membrane thickness for PDMS and EPDM membranes in the separation of toluene/water mixtures. For comparison the results with trichloroethylene/water mixtures for both homogeneous and composite PDMS membranes as well as homogeneous EPDM membranes are also presented in these figures. The data clearly indicate that the permeabilities, obtained from the reciprocal slopes of the lines after linear regression are higher in PDMS than in EPDM, especially for toluene. The determination of the trichloroethylene permeability in PDMS is difficult, due to the small variations in organic component fluxes and the relatively small range of thicknesses investigated. The regression curve in figure 13 is drawn on the basis of the results with composite membranes and one homogeneous membrane. The overall resistance determined for the 17.5 μm membrane was almost identical to the values obtained for the 72 μm composite and the 80 μm homogeneous membrane. Therefore this value was left out of the fitting procedure.



<u>Figure 13:</u> Mass transfer resistances as a function of membrane thickness for PDMS (left) and EPDM (right) membranes

Table 2 summarizes the results obtained for the investigated homogeneous and composite elastomeric membranes. Boundary layer and membrane mass transfer coefficients have also been calculated for the system trichloroethylene/water/OT on the basis of two membrane thicknesses.

The intercepts of the curves, expressing the liquid boundary layer resistances ($1/k_L$), give values of the mass transfer coefficient in the range of 1.4 - 2.5 * 10^{-5} m/s. In principle the liquid boundary layer resistances should be independent of the type of polymer used. The observed deviations are probably due to the extrapolation procedure used. An average liquid boundary layer mass transfer coefficient of (2.0 ± 0.5) * 10^{-5} m/s can be calculated from the values listed in table 2, which is a pretty high, but not an unrealistic value in practical applications.

Table 2: Mass transfer coefficients for elastomeric pervaporation membranes

material	organic component	mass transfer coefficient [m/s] boundary layer	membrane (10 µm)
PDMS (Hom)	toluene	$2.5 * 10^{-5}$	$8.2 * 10^{-4}$
PDMS (Comp)	trichloroethylene	$2.2 * 10^{-5}$	$5.4 * 10^{-4}$
EPDM (Hom)	toluene	$1.4 * 10^{-5}$	$1.1 * 10^{-4}$
EPDM (Hom)	trichloroethylene	$1.7 * 10^{-5}$	$2.8 * 10^{-4}$
OT (Comp)	trichloroethylene	$1.7 * 10^{-5}$	$2.8 * 10^{-4}$

The membrane mass transfer coefficient is dependent of the membrane thickness, but for a 10 µm PDMS membrane this coefficient (k_M) takes a value of $8.2 * 10^{-4}$ m/s for toluene. This indicates that for such a membrane the organic component flux is determined predominantly by the liquid boundary layer resistance and not by the choice of the elastomeric material. Especially for PDMS the contribution of the membrane resistance can almost be neglected. In the case of the more selective EPDM membranes the membrane resistance might become more important.

In this work the attention was focussed on the determination of mass transfer coefficients in the liquid boundary layer and in the membrane respectively from thickness dependent pervaporation measurements. The results of experiments with the boundary layer mass transfer coefficient as the most important variable and the selection of elastomeric membranes through determination of true membrane permeabilities are the subjects of forthcoming papers [18, 19].

2.5 CONCLUSIONS

A resistance-in-series model can be used to determine the mass transfer coefficients in the removal of volatile organic components from water by a pervaporation process.

Under the conditions applied, the resistance of the porous supports used for the preparation of composite membranes was negligible, although no optimization was performed. In this study it is shown that the resistance of the liquid boundary layer can not be neglected in the removal of trace organics from aqueous solutions. The flux of the organic component through the membrane is mainly determined by the liquid boundary layer resistance against mass transfer and only to a minor extent by the choice of the elastomeric material. For elastomers with a lower permeability, such as EPDM, the membrane resistance may become more important. The water flux appears to be inversely proportional to the thickness of the separating layer and it depends strongly on the type of elastomer used. Choosing the elastomer with the highest selectivity seems obvious.

2.6 LIST OF SYMBOLS

A = membrane area [m^2]
$\mathcal{D}$ = diffusion coefficient [m^2/s]
J = total pervaporation flux [m^3/(m^2.s)]
J_i = pervaporation flux of component i [m^3/(m^2.s)]
k = mass transfer coefficient [m/s]
ℓ = membrane thickness [m]
m = weight of collected permeate [kg]
$\mathcal{P}$ = permeability [m^2/s]
S = membrane/liquid solubility coefficient [-]
t = permeation time [s]
w = weight fraction [kg/kg]
x = distance from the membrane wall [m]

<u>Greek symbols</u>

δ = thickness of the liquid boundary layer [m]
ϕ = volume fraction [m^3/m^3]
ρ = liquid density [kg/m^3]

<u>Subscripts</u>

1 = preferentially permeating component
2 = less permeable component
i = component i
L = liquid boundary layer
M = membrane
OV = overall

Superscripts

b = bulk feed solution
c = convection
d = diffusion
f = feed
m = membrane
m,w = membrane wall (in the membrane)
p = permeate
w = membrane wall (in the feed)

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2.8 APPENDIX

The logarithmic function in the film theory relationship:

$$J^p = \frac{\mathscr{D}_L}{\delta} \ln\left(\frac{\phi_1^w - \phi_1^p}{\phi_1^b - \phi_1^p}\right) \tag{6}$$

can be rewritten and rearranged as two separate logarithmic functions.

$$\ln\left(\frac{\phi_1^w - \phi_1^p}{\phi_1^b - \phi_1^p}\right) = \ln\left(\frac{\phi_1^p - \phi_1^w}{\phi_1^p - \phi_1^b}\right) = \ln\left[\left(1 - \frac{\phi_1^w}{\phi_1^p}\right) / \left(1 - \frac{\phi_1^b}{\phi_1^p}\right)\right] =$$

$$= \ln\left(1 - \frac{\phi_1^w}{\phi_1^p}\right) - \ln\left(1 - \frac{\phi_1^b}{\phi_1^p}\right) \tag{A1}$$

Because $-1 < \frac{\phi_1^w}{\phi_1^p} < 1$ and $-1 < \frac{\phi_1^b}{\phi_1^p} < 1$, this equation can be written as a Taylor series:

$$\ln\left(1 - \frac{\phi_1^w}{\phi_1^p}\right) - \ln\left(1 - \frac{\phi_1^b}{\phi_1^p}\right) = \left[- \frac{\phi_1^w}{\phi_1^p} - \left(\frac{\phi_1^w}{\phi_1^p}\right)^2 - \left(\frac{\phi_1^w}{\phi_1^p}\right)^3 - .....\right] - \left[- \frac{\phi_1^b}{\phi_1^p} - \left(\frac{\phi_1^b}{\phi_1^p}\right)^2 - \left(\frac{\phi_1^b}{\phi_1^p}\right)^3 - ....\right]$$

and since $\frac{\phi_1^w}{\phi_1^p} << 1$ and $\frac{\phi_1^b}{\phi_1^p} << 1$, powers of two and higher can be neglected and the logarithmic function given in equation (A1) is converted to:

$$\ln \left(\frac{\phi_1^w - \phi_1^p}{\phi_1^b - \phi_1^p}\right) = \frac{\phi_1^b - \phi_1^w}{\phi_1^p} \qquad \text{(A2)}$$

Combination of equations (6) and (A2) gives a simple equation for the mass transfer in dilute solutions:

$$J^p.\delta = \mathcal{D}_1 \frac{\phi_1^b - \phi_1^w}{\phi_1^p} \qquad \text{(A.3)}$$

Combination of equations (4), (A.3) and substitution of $\mathcal{D}_L/\delta$ by the generally used mass transfer coefficient k_L gives:

$$J_1^p = k_L\,(\phi_1^b - \phi_1^w) \qquad \text{(A.4)}$$

CHAPTER 3

RESISTANCES IN SERIES: BOUNDARY LAYER EFFECTS

H.H. Nijhuis, M.H.V. Mulder and C.A. Smolders

SUMMARY

The influence of the hydrodynamic resistance on the removal of toluene and trichloroethylene from binary aqueous solutions by pervaporation has been studied. A resistance-in-series model and mass transfer correlations have been used to describe the observed concentration polarization phenomena. To vary the resistance of the membrane, various elastomeric membranes have been used with different effective thicknesses. Mass transfer coefficients have been determined for laminar flow in a flat channel cell as well as laminar and turbulent flow in a stirred cell. The "simple liquid film model" in which the resistance of the membrane to mass transfer is neglected appears to be inadequate to describe the overall transport. In order to calculate the membrane resistance, membrane permeabilities are used, determined from actual pervaporation measurements. Liquid boundary layer mass transfer coefficients upto values of 6.10^{-5} m/s follow from Sherwood relations. Reasonable accurate predictions of the overall mass transfer coefficient in the pervaporation process are observed in the stirred cell configuration and for laminar flow conditions in the flat channel cell.

3.1 INTRODUCTION

Much research and development efforts in membrane processes are directed primarily to improving membrane performance, both in terms of selectivity and flux. With respect to this the development of thin film composite membranes [1] with improved performance can be considered as a break-through. Starting point for commercialization of membrane processes is the availability of high performance membranes. After development of these high flux/high selectivity membranes the process conditions should be considered more carefully in order to describe concentration polarization phenomena and membrane fouling. Concentration polarization phenomena are inherent to membrane separation processes. However, the extent of this phenomenon may vary drastically depending on the membrane process and the application. Although these phenomena are already very well known from traditional membrane filtration processes like micro-, ultra- and hyperfiltration, until recently only little attention has been paid to boundary layer effects in gas separation, vapor separation and pervaporation [2-9].

The development of physical models describing the transport in the boundary layer is therefore essential. Most of the work concerning boundary layer effects has been carried out in the field of ultrafiltration. Most models require knowledge of the boundary layer mass transfer coefficient. Although alternative relations have been suggested, a combination of the liquid film model and mass transfer correlations has proven to be most successful in describing the transport rates at the membrane interface [10]. Goldsmith [11] used three different ultrafiltration systems with increasing membrane area to examine the parameters that determine ultrafiltration rate and selectivity. Boundary layer mass transfer coefficients were calculated for a stirred cell, a flat channel cross-flow cell and a tubular membrane module and these values were compared qualitatively with mass transfer correlations from literature. Strathmann [12] derived a theoretical equation for the concentration increase at the membrane interface for turbulent and laminar flow in a rectangular cell and laminar flow in a stirred cell on the basis of a simple rejection equation, the liquid film model and heat transfer analogies. The concentration increase at the membrane interface could be predicted with reasonable accuracy. Other interesting papers on mass transfer correlations are that of Wiley and coworkers [13], who carried out a theoretical study on the optimization of membrane module design, of Nakao and Kimura [14], who compared experimental values from the velocity variation method with theoretical values following Sherwood correlations and of Porter [15], who correlated ultrafiltration fluxes with recirculation rates.

The aim of the present work is to investigate the effect of the boundary layer resistance on pervaporation performance. Data for laminar flow in a flat cross-flow stainless steel cell and for laminar and turbulent flow in a stirred cell will be presented. A theoretical model will be described and experimentally determined overall mass transfer coefficients will be compared with model predictions.

3.2 THEORY

3.2.1 General

In membrane filtration processes the membrane is in direct contact with a feed mixture. As a result of an applied driving force one or more components permeate selectively through the membrane. As a result of this permeate flux mass transfer of the components in the feed mixture will occur as a convective flux. Furthermore a diffusion process is generated. After some time a steady state will be established with a constant concentration profile (see figure 1). The less permeable components diffuse back into the feed mixture, whereas the preferentially permeating components diffuse from the bulk feed solution to the membrane interface.

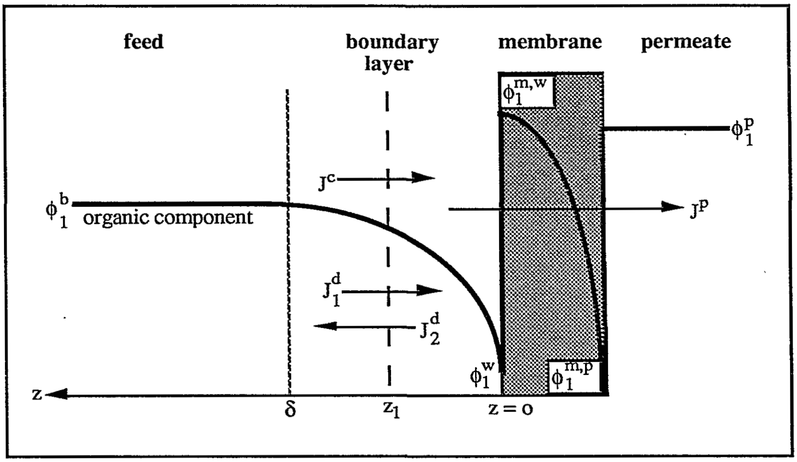

Figure 1: Concentration profile for the preferentially permeating component

Previously [16] it was shown how an overall mass transfer equation based on the film theory relationship for the preferentially permeating organic component can be derived. The permeability of a component through the membrane can either be expressed in terms of a combination of solubility coefficient and diffusion or in terms of a mass transfer coefficient. Although the use of diffusion coefficients presents a way to describe the concentration profile in the subsequent layers, here transport rates have been described in terms of mass transfer coefficients. The mass transfer coefficient k [m/s] represents the proportionality factor between the flux and the driving force. In this case a concentration difference and it is equal to the ratio of diffusion coefficient ($\mathcal{D}$) and diffusion length (ℓ). The two basic equations in the so called mass transfer resistance-in-series model are given below.

In the case of zero concentration at the permeate side of the membrane an overall equation for the flux of component 1 can be given:

$$J_1^p = k_{OV} \cdot \phi_1^b \tag{1}$$

The overall mass transfer coefficient k_{OV}, can simply be determined from measurements of the feed concentration and the steady state permeate component flux in the pervaporation experiments. According to a resistance model the overall mass transfer coefficient (k_{OV}) is related to the mass transfer coefficients in the membrane and the boundary layer respectively by:

$$\frac{1}{k_{OV}} = \frac{1}{k_L} + \frac{1}{k_M} = \frac{1}{k_L} + \frac{\ell}{\mathcal{D}_i^m . S_{M/L}} = \frac{1}{k_L} + \frac{\ell}{\mathcal{P}} \tag{2}$$

This equation was used previously [16] to determine the permeability coefficient ($\mathcal{P}$). Therefore the overall mass transfer resistance ($1/k_{OV}$) in steady state pervaporation experiments at identical flow conditions was determined as a function of the membrane thickness (ℓ). As can be seen from equation (2) a plot of $1/k_{OV}$ vs. ℓ gives the intercept $1/k_L$ and the slope $1/\mathcal{P}$. In the present work the contribution of the boundary layer resistance ($1/k_L$) has been investigated further.

3.2.2 Mass transfer correlations

The overall resistance is composed of a boundary layer resistance ($1/k_L$) and a membrane resistance ($1/k_M$) in series. As was shown above k_L can be determined if k_{OV} and k_M are known. The mass transfer coefficient (k_L) in the liquid boundary layer can also be obtained from semiempirical correlations. These Sherwood relations in general represented as:

$$Sh = \frac{k_L \cdot d_h}{\mathcal{D}} = p \cdot Re^q \cdot Sc^r \cdot \left(\frac{d_h}{L}\right)^s \tag{3}$$

give the mass transfer coefficient (k_L) as a function of the dimensions of the module, the Reynolds number (Re) and the Schmidt number (Sc):

$$Re = \frac{\rho \cdot v \cdot d_h}{\eta} \tag{4}$$

$$\mathrm{Sc} = \frac{\eta}{\rho \cdot \mathscr{D}} \tag{5}$$

Mass transfer coefficients are separately described for laminar and turbulent flow conditions. In literature many different values for p, q, r and s can be found depending on operating conditions. For laminar flow conditions in straight channels (Re < 2000) the Graetz-Leveque equation is the most commonly known.

(Graetz - Leveque [17]) $$\mathrm{Sh} = \frac{k_L \cdot d_h}{\mathscr{D}} = 1.85 \cdot \mathrm{Re}^{0.33} \cdot \mathrm{Sc}^{0.33} \cdot \left(\frac{d_h}{L}\right)^{0.33} \tag{6}$$

The Graetz-Leveque equation has a sound theoretical basis and should therefore be preferred for calculating boundary layer mass transfer coefficients.

In a stirred pervaporation cell the circumstances deviate strongly from those in a flat channel cell or a tube. Several authors in the field of membrane filtration [11, 12, 18] referred to the work of Smith et. al. [19] in which a comprehensive description of the mass transfer in stirred cells using Sherwood correlations is given. The Reynolds number is related to the stirring speed of the impeller (ω) by:

$$\mathrm{Re} = \frac{\rho \cdot \omega \cdot b^2}{\eta} \tag{7}$$

For laminar and turbulent flow respectively in a stirred cell the following equations have been determined experimentally by these authors:

laminar regime (Re < 32,000) $$\mathrm{Sh} = \frac{k_L \cdot b}{\mathscr{D}} = 0.29 \cdot \mathrm{Re}^{0.57} \cdot \mathrm{Sc}^{0.33} \tag{8}$$

turbulent regime (Re > 32,000) $$\mathrm{Sh} = \frac{k_L \cdot b}{\mathscr{D}} = 0.044 \cdot \mathrm{Re}^{0.75} \cdot \mathrm{Sc}^{0.33} \tag{9}$$

In equations (8) and (9) b represents the radius of the cell. For other cell geometries correction factors have to be used. Boundary layer mass transfer coefficients decrease as the distance between impeller and membrane interface is increased or impeller size and cell size deviate strongly.

All the independent parameters in the above equations (6, 8, 9) can be measured (d_h, L) or easily obtained from handbooks (η, ρ). The value for the diffusion coefficient, however, is more difficult to obtain. In literature [20] several equations have been proposed to relate the mutual diffusion coefficient to composition, e.g. the Darken equation [21].

$$\mathcal{D}_{ij} = (\mathcal{D}_i^*.x_i + \mathcal{D}_j^*.x_j).([\delta \ln a / \delta \ln x]_{T,P}) \qquad (10)$$

where $\mathcal{D}_i^*$ and $\mathcal{D}_j^*$ are tracer diffusion coefficients at the mole fractions x_i and x_j. The correction term for the activity of the components in the mixture is evaluated at the same concentrations. The unavailability of tracer diffusion coefficients in most instances has led to the development of alternative equations, e.g. the Vignes relation [22]:

$$\mathcal{D}_{ij} = [(\mathcal{D}_{ij}^0)^{x_j} . (\mathcal{D}_{ji}^0)^{x_i}].([\delta \ln a / \delta \ln x]_{T,P}) \qquad (11)$$

This equation is often easier to use because diffusion coefficients for infinite dilution may be estimated by several techniques and models, e.g. the Wilke-Chang equation.

The high dilution and poor solubility of the organic component in water makes a drastic simplification of the composition dependent diffusion equations valid. Activity coefficients can be estimated on the basis of mutual solubility data [20]. For the calculation of activity coefficients over the entire range of composition in the homogeneous regions it is necessary to choose some thermodynamically consistent analytical expression which relates these two parameters. In literature many different models are commonly used, e.g. the van Laar, the Wilson, the NRTL and the UNIQUAC model. Using either one of these equations will show that the activity coefficients in this range of solubility are practically independent of the composition. Therefore the mutual diffusion coefficient $\mathcal{D}_{ij}$ equals the diffusion coefficient at infinite dilution ($\mathcal{D}_{ij} = \mathcal{D}_{ij}^0$).

The value of the diffusion coefficient at infinite dilution can be obtained with reasonable accuracy from the Wilke-Chang equation [23], given below:

$$\mathcal{D}_{i,j}^0 = \frac{7.4 * 10^{-15} . (\psi_j . M_j)^{1/2} . T}{\eta_j . V_i^{0.6}} \qquad (12)$$

In this equation ψ represents the so called association parameter [-], which is 2.6 in the case of water, M_j is the molecular weight of component j [g/mole] and V_i the molar volume of component i at the boiling point [cm^3/mole]. In the original Wilke-Chang equation the dynamic viscosity was given in centiPoise [cP], whereas the dimension for the diffusion coefficient was [cm^2/s]. The original equation has been modified to units used in this work yielding equation (12). The subscripts i and j refer to the organic component and water respectively. Values for V_i can either be obtained from extensive tabulations or can be estimated from group contribution methods [20]. A value of 95.2 cm^3/mole was calculated for trichloroethylene, whereas for toluene a value of 118.7 cm^3/mole is obtained. For aqueous solutions of respectively toluene and trichloroethylene binary liquid diffusion coefficients at infinite dilution of $9.6 * 10^{-10}$ m^2/s and $1.1 * 10^{-9}$ m^2/s can be calculated from equation (12).

With the set of equations (1, 2, 6, 8, 9) the transport in the boundary layer can be described, provided that the essential physical properties (viscosity, density, diffusion coefficient) of the feed mixture are known. In combination with an appropriate model and permeability data for the transport in the membrane, flux and selectivity for the overall membrane separation process can be predicted for these highly selective separations of aqueous solutions by pervaporation in a stirred cell or in a straight channel.

3.3 EXPERIMENTAL

3.3.1 Materials

Polysulfone (PSF; Udel P1700) has been used for the preparation of the porous support in composite membranes. Polydimethylsiloxane (PDMS; RTV 615 A) and crosslinking agent (RTV 615 B) are purchased from General Electric and have been used for the preparation of dense homogeneous membranes and for the toplayer in composite membranes. Ethylene Propylene Rubber (EPDM, Keltan 578, DSM) and polyoctenamer (OT, Vestenamer 8012, Hüls) have been used for the preparation of dense homogeneous membranes.

The solvents (analytical grade) and the crosslinking agent dicumylperoxide (DCP) are purchased from Merck. The chemicals were used without further purification.

Water for the pervaporation experiments is deionized and ultrafiltrated before use. In order to homogenize the demixed permeate we used ethanol of analytical grade which was dried on molecular sieves.

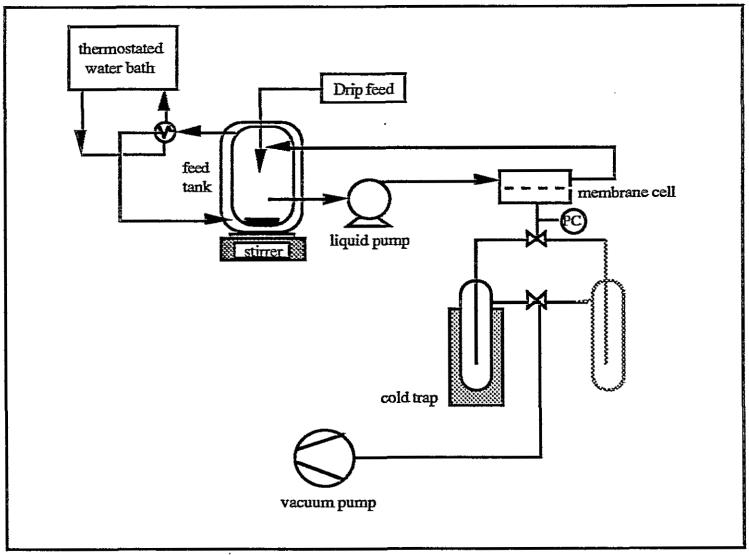

Figure 2: Schematic representation of the experimental set-up for pervaporation

3.3.2 Membrane preparation and characterization

Three different polymer materials have been selected on the basis of a previous study [24]. Silicone rubber (PDMS) is selected because of the extremely high permeation rates for several penetrants. Ethylene propylene rubber (EPDM) and polyoctenamer (OT) have been investigated, because an extremely high selectivity towards the organic component is combined with a reasonable organic component flux. Both dense homogeneous and composite membranes with an elastomeric permselective toplayer have been prepared as described previously [16].

The porous support, the composite membranes and the dense homogeneous peroxide cured membranes were characterized by standard procedures [16]. The effective thicknesses of the membranes ranged from 5 µm for a composite PDMS membrane to 200 µm for a homogeneous OT membrane.

3.3.3 Pervaporation experiments

Pervaporation experiments at 25 °C have been carried out with a standard laboratory pervaporation set-up as schematically represented in figure 2. Compared to previous studies [16], in which a more detailed description of the experimental apparatus is given, two other cell configurations were used in the present work. Schematic drawings of a rectangular cross-flow cell, used at Reynolds numbers smaller than 1000, and a stirred pervaporation cell for Reynolds numbers upto 80,000 are given in figure 3 and 4 respectively.

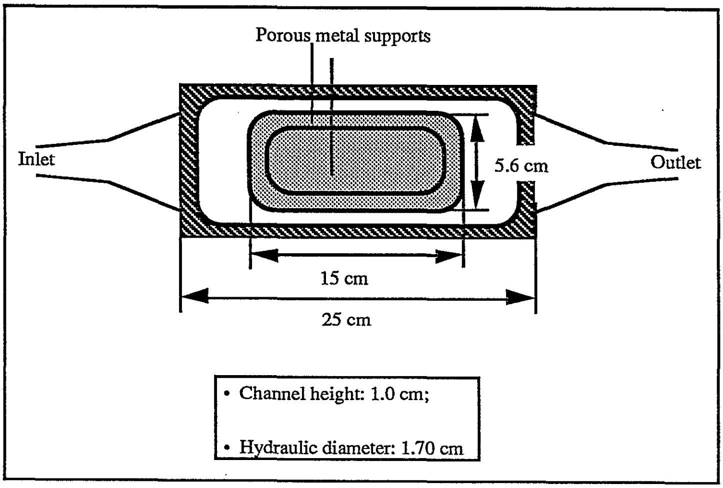

Figure 3: Schematic drawing of the flat channel pervaporation cell

The cross-flow pervaporation cell has the possibility of withdrawing the permeate both from the center and from the sides of the cell. In this way the occurrence of side-effects could be determined. Such effects, however, have not been observed and the collected permeates were treated separately to obtain duplo flux values, determined according to the following equation:

$$J_i^p \cdot \rho_i = \frac{m}{A \cdot t} \cdot w_i^p \qquad (13)$$

The pervaporation experiments were performed in such a way that the feed concentrations remain constant. As a standard procedure toluene/water mixtures have been used with a concentration of 250 μg/g. The effect of lower concentrations on the pervaporation performance has been studied using trichloroethylene/water mixtures with concentrations of 2 and 4 μg/g.

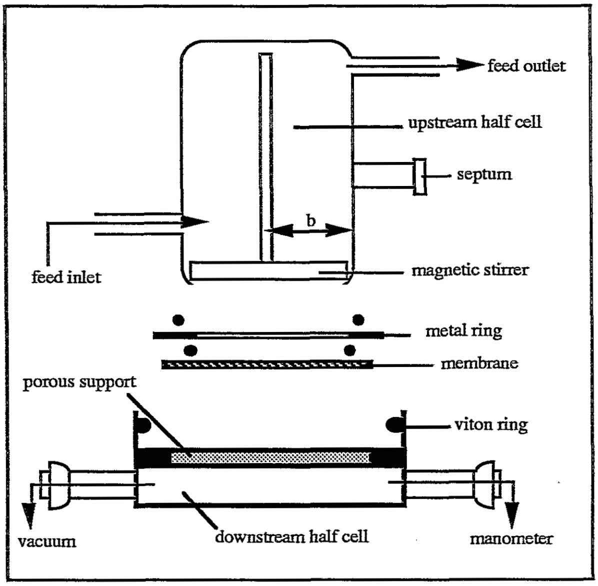

Figure 4: Schematic drawing of the stirred pervaporation cell

3.4 RESULTS AND DISCUSSION

The problem of concentration polarization in the removal of trace organics from water is already known from literature. Psaume and coworkers [2] performed experiments with a Silastic® medical grade tubings module and described the concentration difference at module entrance and exit in very dilute aqueous solutions of trichloroethylene (50 - 250 μg/l). According to the authors the theoretical model, based on the liquid film theory and the Graetz-Leveque equation, predicts with reasonable accuracy the performance of the pervaporation module. Côté and Lipski [3] used a similar pervaporation module and studied the separation of aqueous solutions of carbon tetrachloride, trichloroethylene and phenol (30 ppm) at higher Reynolds numbers, though still in the laminar region. These authors extended the "simple film model" developed by Psaume et. al., in which the membrane resistance is neglected, to a "resistance-in-series model". A contribution of the membrane to the overall resistance could be shown at higher cross-flow velocities on a theoretical basis. Such a clear contribution of the membrane to the overall resistance could experimentally not be shown in their experiments due to the low Reynolds numbers established.

In this section first the results of experiments with the rectangular cross-flow pervaporation cell operating at low Reynolds numbers will be given. Experimentally determined overall mass transfer coefficients will be compared to values obtained from the Graetz-Leveque equation. In addition the results of the experiments with a stirred cell configuration will be discussed. In comparison with the flat channel cell higher boundary layer mass transfer coefficients could be established.

Table 1: Characteristic data and values used in the calculation of theoretical mass transfer coefficients for the flat channel cell

Feed solution	
Diffusion coefficient (toluene/water)	$9.6 * 10^{-10}$ m²/s
Diffusion coefficient (tri/water)	$1.1 * 10^{-9}$ m²/s
Dynamic viscosity	$0.89 * 10^{-3}$ kg/m.s
Density	997 kg/m³
Flat channel cell	
Hydraulic diameter	0.017 m
Length	0.15 m
Membrane (PDMS)	
Toluene permeability	$8.2 * 10^{-9}$ m²/s
Membrane thickness	125 μm

3.4.1 Cross-flow pervaporation

The results obtained with the flat channel pervaporation cell for the separation of toluene/water mixtures with a PDMS membrane for low laminar flow conditions (Re < 1000) are given in figure

5. The Graetz-Leveque equation, represented by the dotted line, predicts already with reasonable accuracy the experimental overall mass transfer coefficients, represented by the closed circles. At these low cross-flow velocities the resistance of the membrane to mass transfer can be neglected as indicated by the small difference between the dotted line and the solid line, the latter representing the model prediction including membrane resistance. Characteristic data used to calculate the theoretical mass transfer coefficients are given in table 1.

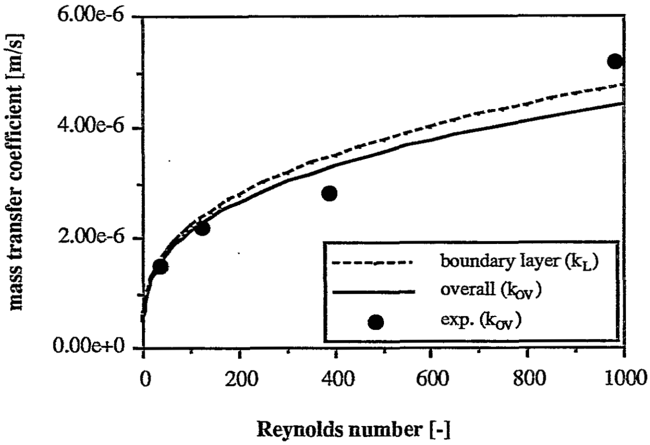

Figure 5: Experimental overall mass transfer coefficients and model predictions for a flat channel pervaporation cell in the laminar regime

Important criterium with respect to the applicability of certain mass transfer correlations is the inlet length of the module. The dimensions of the flat channel cell were such as to prevent a concentration drop over the length of the cell. Therefore a relatively short cell with a relatively large slit height was used in our investigations. With increasing Reynolds number the inlet length will be of increasing importance [25] and the observed and theoretical mass transfer coefficients will deviate. The stirred cell has a configuration in which high liquid boundary layer mass transfer coefficients can be established, whereas a constant concentration in the bulk feed solution above the membrane is maintained. Pervaporation experiments performed with a continuous stirred cell are discussed below.

3.4.2 Stirred cell pervaporation

Mass transfer correlations for stirred cells are already known since the 1930's, when Chilton and Colburn [26] made use of the analogy between heat and mass transfer. However, a large number of these semi-empirical correlations are found in literature with different dependencies on both stirring speed and diffusion coefficients. The most commonly used value of the power dependence for the Schmidt number is 0.33, although also other values have been reported, which were criticized later [27]. The determination of the power dependence for the Reynolds number and the value for the proportionality factor p has been discussed in several papers [11, 12, 18, 28].

Smith and coworkers studied the role of cell geometry on the dissolution rate from a rigid interface of benzoic acid [19]. The liquid boundary layer mass transfer coefficient determined from these experiments was used to describe the transport behaviour in a dialysis cell. Their cell dimensions agree very well with the dimensions of the pervaporation cell used by the present authors as indicated in table 2, which allows the use of their correlations without further geometry corrections.

Table 2: Comparison of stirred cell dimensions

Cell geometry		Pervaporation cell	Dialysis cell [19]
Four blade impeller:	Diameter blades [cm]	5.8	5.68
	Height blades [cm]	0.71	0.64
Upstream cell:	Vessel diameter [cm]	6.2	6.30
Gap widths:	Distance membrane - impeller [cm]	0.23	0.31
	Distance impeller - vessel wall [cm]	0.3	0.32

The dependence of flux on stirring rate was determined, using different membranes and different fixed concentrations of the liquid mixture. The correlations given in the theoretical part, equations (8) and (9), will be used to calculate theoretical liquid boundary layer mass transfer coefficients. The relevant physical properties of the feed solution and their values are summarized in table 1, whereas the characteristic data for the membranes used, are given in table 3. In figure 6 the overall mass transfer coefficient in the separation of toluene/water mixtures with a composite silicone rubber membrane is given as a function of the Reynolds number.

Table 3: Permeability coefficients and thicknesses of the investigated membranes

PDMS (composite)	
Permeability coefficient (toluene)	$8.2 * 10^{-9}$ m^2/s
Effective membrane thickness	5.4 µm
EPDM (homogeneous)	
Permeability coefficient (toluene)	$1.1 * 10^{-9}$ m^2/s
Membrane thickness • EPDM 1	35 µm
• EPDM 2	40 µm
OT (homogeneous)	
Permeability coefficient (trichloroethylene)	$2.8 * 10^{-9}$ m^2/s
Membrane thickness: • OT 1	200 µm
• OT 2	50 µm

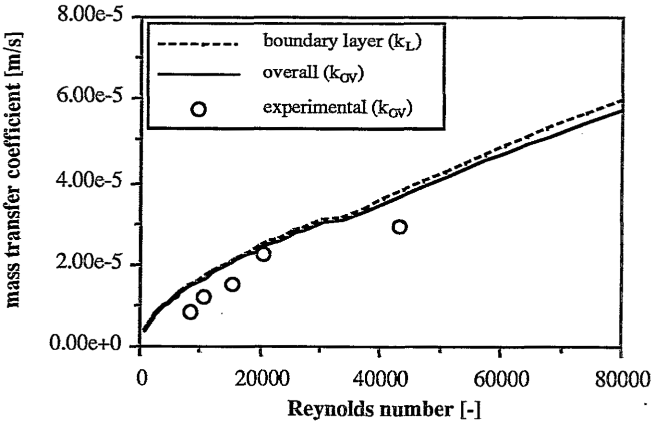

Figure 6: Overall mass transfer coefficients in a stirred pervaporation cell using a composite PDMS membrane ($\ell_{eff} \approx 5$ µm) for binary toluene/water mixtures (250 µg/g)

The theoretical (solid) line predicts with reasonable accuracy the experimental overall mass transfer coefficients given as the open circles in figure 6. From the very small difference between the solid line and the dotted line, which represents the theoretical boundary layer mass transfer coefficient it is clear that the resistance to mass transfer of the membrane can be neglected in this case. Furthermore the influence of the porous support on the overall mass transfer resistance towards the organic component is small as can be derived from the small difference between experimental and theoretical values.

In figure 7 similar results are given for ethylene propylene rubber (EPDM). The high selectivities in the removal of trace organics from water makes EPDM a very interesting membrane material [24]. The lower permeabilities (in comparison with PDMS) increases the contribution of the membrane to the overall resistance against mass transfer. Two dense homogeneous membranes with almost identical thicknesses have been investigated. The overall mass transfer coefficients determined from steady state pervaporation experiments are given in figure 7 as the closed and open triangles for the two membranes investigated. The solid line represents the model fit for the overall mass transfer coefficient, whereas the dotted line represents the contribution of the liquid boundary layer alone.

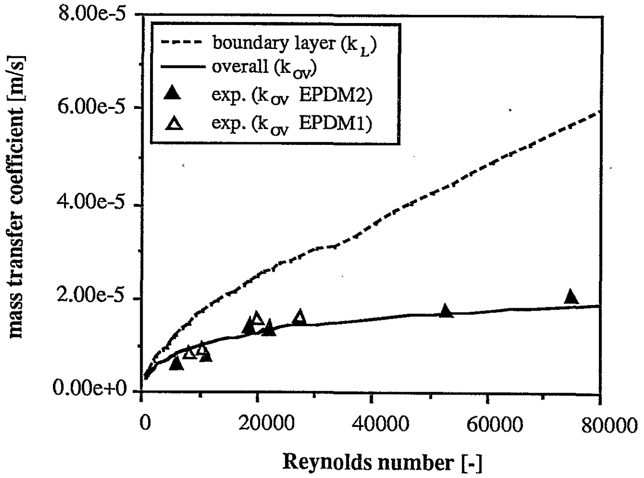

Figure 7: Overall mass transfer coefficients in a stirred pervaporation cell using homogeneous EPDM membranes (40 μm) for toluene/water mixtures (250 μg/g)

The accuracy of the model fit appears to be even better than in the previous investigated system (see figure 6). A plateau value seems to have been reached, indicating that the resistance of the membrane to mass transfer becomes dominant and the flux of the organic component cannot be improved any further by increasing the stirring speed. As can be seen from figure 7, an increase of the boundary layer mass transfer coefficient (k_L) to values above $2 * 10^{-5}$ m/s will not improve the flux of the organic component. In this case an organic component flux increase can only be established by decreasing the effective membrane thickness. Due to the poor mechanical strength of homogeneous elastomeric membranes with thicknesses smaller than 40 μm, composite membranes are preferred.

The validity of the resistance-in-series model was also verified in the low ppm-range. In this case dense homogeneous polyoctenamer (OT) membranes were investigated with thicknesses of 50 and 200 μm, whereas the concentrations in the liquid feed mixtures were 2 and 4 μg/g respectively. Again the solid line and the dotted line are the model predictions with respect to the overall and the boundary layer mass transfer coefficient respectively. The closed squares and open squares represent the experimental overall mass transfer coefficients for the two membranes with different thicknesses.

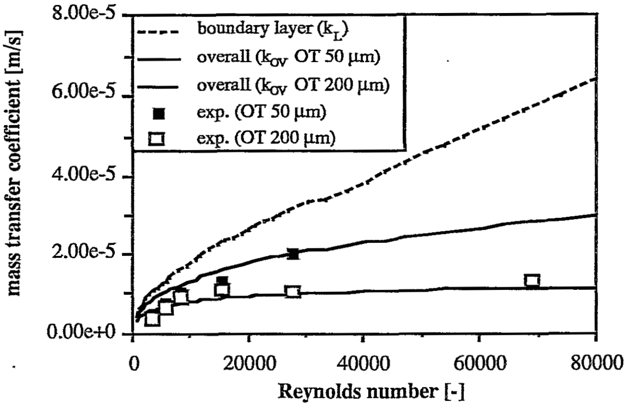

Figure 8: Overall mass transfer coefficients in a stirred pervaporation cell using homogeneous OT membranes (50 and 200 μm) in the separation of trichloroethylene/water mixtures (2 and 4 μg/g)

Again the combination of a resistance-in-series model and mass transfer correlations gives a good prediction of the experimentally determined mass transfer coefficients in the lower ppm-range. It is obvious that for the thick OT membrane a plateau value is already reached at a Reynolds number of 20,000, indicating that the resistance of the relatively thick OT membranes dominates the transport of the organic component in the pervaporation process. For the thinner OT membrane the boundary layer resistance will become increasingly important, but still the membrane resistance plays an important role in the range of Reynolds numbers investigated.

From figures 6 to 8 it can be concluded that the stirred cell appears to be an appropriate configuration to study boundary layer effects in the pervaporation of trace organics from water, provided that a proper mass transfer correlation is available. In combination with the resistance-in-series model suggested by Côté and Lipski [3] and the permeabilities obtained from earlier work [16] overall mass transfer coefficients and organic component fluxes can be predicted quite accurately.

3.4.3 Considerations on module design

In the previous section experimental and theoretical overall mass transfer coefficients have been determined and compared with each other. To indicate the strong effect of the liquid boundary layer mass transfer coefficient on the overall transport, the model is used to predict organic component fluxes for EPDM and PDMS membranes with thicknesses of respectively 2, 10, 20 and 40 μm in the separation of toluene/water mixtures.

The increasing importance of the boundary layer mass transfer coefficient with decreasing membrane thickness is clearly shown in figure 9. For 2 μm membranes in both cases an almost linear increase with the boundary layer mass transfer coefficient is observed. At values of the boundary layer mass transfer coefficient above 2.10^{-5} m/s the resistance of a 40 μm EPDM membrane is of predominant importance with respect to the mass transfer of the organic component. This is in direct contrast with PDMS membranes for which a strong improvement of organic component fluxes is observed over the entire range shown. Furthermore it can be concluded that with respect to the organic component flux for PDMS membranes the thickness of the membrane is of minor importance. Only small differences in toluene fluxes are observed for these membranes in contrast to EPDM membranes for which the toluene fluxes can differ by a factor of 2 to 3 at high boundary layer mass transfer coefficients.

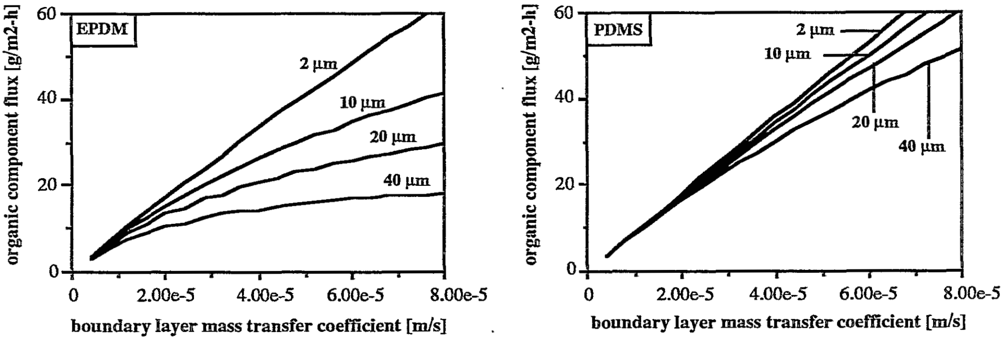

Figure 9: Theoretical organic component fluxes vs. the boundary layer mass transfer coefficient for EPDM (left) and PDMS (right) membranes of various membrane thicknesses

The model can also be very useful to estimate the factors that are important in relation to the optimization of the pervaporation module performance. Such an optimization procedure is a very elaborate task in which a large number of parameters should be considered and carefully evaluated. Some of these parameters are the required membrane area, the frictional pressure drop both at the upstream side and on the downstream side of the membrane, the tendency of fouling and possible heating of the feed mixture (to increase diffusion coefficients and reduce the viscosity of the feed mixture). Furthermore several cost factors have to be taken into account: e.g. the condensation costs, the membrane costs and the module costs.

Due to the low fluxes established reheating of the feed mixture is not a strict necessity, whereas pressure losses at the permeate side will probably be of minor importance when the module is carefully designed with respect to this factor. Pervaporation is an activity driven process, which implies that pressure losses are only important with respect to the feed energy costs. The total costs to operate the process are affected only to a limited extent by this cost factor.

In this particular case, in which the membrane mass transfer coefficient is quite large, and other process parameters are of minor importance, the basic approach is that the mass transfer coefficient (k_L) should be increased at minimum costs. From the general equation (3) the parameters can be evaluated which are the most important with respect to diffusion limitations in the feed mixture.

The strongest dependency is shown on the hydraulic diameter. For laminar flow the boundary layer mass transfer coefficient is inversely proportional to this parameter. In the turbulent region a stronger dependency on the hydraulic diameter is observed.

However, the boundary layer mass transfer coefficient cannot be increased to extremely high values, because this would also involve a very strong increase in energy consumption. This energy consumption is related to the product of feed flow rate and the pressure drop in the channel, which is on its turn related to the length of the module as given in the following equation.

Frictional pressure drop: $$P_f = \frac{2 \,.\, f \,.\, \rho \,.\, L \,.\, \overline{v^2}}{d_h} \qquad (14)$$

With respect to the energy consumption short modules are advantageous with large channel diameters. At this point an optimization procedure will be essential to determine the optimal fiber diameter. Because the liquid feed pump energy costs in pervaporation processes are often of only minor importance in comparison with module and membrane costs [29] short fibers with a small diameter should be preferred.

The reflections given above merely aim to present qualitative indications of the parameters which affect the liquid boundary layer mass transfer coefficient. A careful evaluation of all the parameters involved and subsequent optimization of the pervaporation performance falls beyond the scope of this work. Some of these aspects, however, are considered in a forthcoming paper [29].

3.5 CONCLUSIONS

Experimental results for cross-flow in the laminar regime (Re < 1000) in a rectangular pervaporation cell with large slit height show that the resistance contribution of a homogeneous PDMS membrane (125 μm) to the overall resistance in pervaporation can be neglected.

For the stirred cell configuration large liquid boundary layer mass transfer coefficients could be established. For the homogeneous membranes used in the investigations the membrane resistance is of increasing importance with respect to the overall mass transfer resistance. From the resistance-in-series model using membrane permeability values in combination with mass transfer correlations, predictions for the overall mass transfer coefficient of the organic component can be obtained with reasonable accuracy. The model clearly indicates the increasing contribution of the less permeable (but highly selective) EPDM membranes to the overall mass transfer resistance with increasing boundary layer mass transfer coefficient in comparison with the PDMS membranes.

For optimization of the pervaporation performance various parameters have to be carefully evaluated. With respect to the liquid boundary layer mass transfer coefficient, in general small diameters of the fibers, tubes or channels should be favoured. In the laminar regime the length of the module also plays an important role. However, with respect to the energy consumption short modules are advantageous with large channel diameters.

3.6 LIST OF SYMBOLS

A = membrane area [m^2]
a = activity [-]
b = radius of the stirred cell [m]
d_h = hydraulic diameter [m]
$\mathcal{D}$ = diffusion coefficient [m^2/s]
$\mathcal{D}^*$ = tracer diffusion coefficient [m^2/s]
$\mathcal{D}^0$ = diffusion coefficient for infinite dilution [m^2/s]
f = Fanning friction factor [-]
J_i = volume pervaporation flux of component i [$m^3/(m^2.s)$]
k = mass transfer coefficient [m/s]
L = module length [m]
ℓ = membrane thickness [m]
M = molecular weight [g/mol]
m = weight of collected permeate [kg]
n = number of fibers [-]
P_f = pressure loss [Pa]
$\mathcal{P}$ = permeability [m^2/s]
p = Sherwood correlation constant [-]
Q = flow rate [m^3/s]
q = Sherwood correlation constant [-]
Re = Reynolds number [-]
r = Sherwood correlation constant [-]
Sc = Schmidt number [-]
Sh = Sherwood number [-]
s = Sherwood correlation constant [-]

T = temperature [K]
t = permeation time [s]
V = molar volume at the boiling point [cm^3/mole]
v = flow velocity [m/s]
w = weight fraction [g/g]
x = mole fraction [mole/mole]

Greek symbols
ϕ = volume fraction [m^3/m^3]
η = dynamic viscosity [kg/m-s]
ν = kinematic viscosity [m^2/s]
ρ = density [kg/m^3]
ω = impeller rotational velocity [rad/s]
ψ = association parameter for the solvent [-]

Subscripts
i = component i
j = component j
1 = preferentially permeating component
L = liquid boundary layer
M = membrane
OV = overall

Superscripts
b = bulk feed solution
p = permeate

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CHAPTER 4

PERMEABILITIES OF ELASTOMERIC MEMBRANES

H.H. Nijhuis, M.H.V. Mulder and C.A. Smolders

SUMMARY

A wide range of homogeneous elastomeric membranes has been prepared using dicumylperoxide as a general crosslinking agent. The membranes were used in the removal of volatile organic components from aqueous solutions by pervaporation. Pervaporation experiments have been performed under identical hydrodynamic conditions in order to fix the boundary layer mass transfer coefficient at a constant and known value. For comparison of the permeabilities of different pervaporation membrane materials this is of utmost importance. A wide range of selectivity factors upto a value of 100,000 is obtained, whereas usually the permeabilities for the organic component are in the range of 10^{-10} - 10^{-9} m^2/s *and* 10^{-14} - 10^{-12} m^2/s *for water.*

The permeability data obtained for the various elastomers have been related to the chemical and physical nature of the elastomers through the solubility parameter and the glass transition temperature respectively. Both diffusional and sorption effects seem to be important, determining the water transport behaviour in the elastomeric membranes. Differences in the permeabilities of the organic component can primarily be ascribed to structural parameters in the membrane material, like degree of unsaturation and presence of steric side groups.

4.1 INTRODUCTION

For the specific removal of volatile low molecular weight organics from aqueous solutions, pervaporation offers excellent possibilities to compete with alternative techniques like adsorption onto activated carbon, air stripping and biological treatment.

Biological treatment has generally the disadvantage of being a slow and not always very effective process. Air stripping and adsorption are proven processes, but have the disadvantage that the pollutant is transferred to a second phase, where a similar separation problem, on a smaller scale, remains. The attractiveness of pervaporation lies in the fact that the polluting compounds are selectively removed from the feed as an almost pure liquid. Possible applications for the pervaporation process can be found for example in surface or ground water treatment. Furthermore this membrane process can be integrated in existing industrial processes, like the treatment of aqueous waste streams in the petrochemical off-shore industry.

Probably the first publication describing the extraction of contaminants from dilute aqueous solutions by pervaporation came from Cole and Genetelli [1]. They studied the removal of ammonia using polypropylene, dacron (polyacrylonitrile) and nylon (polyamide) hollow fiber modules and stated that although very large surface areas are required for this particular application, pervaporation is very promising in the treatment of industrial wastes containing volatile organic components. This statement was confirmed a few years later, when silicone rubber membranes proved to be very helpful for analytical applications in enriching dilute aqueous solutions and air contaminated with volatile organic impurities [2-3]. Since then several studies have been performed, in which the pervaporation behaviour of different polymers in the removal of volatile organics from water has been investigated [3-7]. Elastomers seem to have the greatest potential in this field. The reason for this fact can be explained already qualitatively with the solution-diffusion model [8-9]. The relatively simple manufacture of the silicone rubber membranes and the high permeability for the organic component resulted in an increase of research in vapour recovery and treatment of aqueous solutions using this elastomer. There are, however, indications that other elastomers could have a better potential in this field [10-11].

Fluxes as measured with relatively thick homogeneous membranes in gas/vapor separation and pervaporation can generally be improved by the use of composite membranes consisting of a thin selective toplayer on a porous support [12-14]. In pervaporation of volatile organics several investigators indicated the existence of a liquid boundary layer [15-17], causing a strong decrease in pervaporation selectivity.

From these considerations it can be concluded, that three layers in series can be defined, which may contribute to the performance of pervaporation processes using composite pervaporation membranes.

- A porous support with a finite but low resistance towards the permeating organic component
- A permselective toplayer, which performs the actual separation
- A liquid boundary layer, which inherently exists in mass transfer operations.

Membrane development is important to reduce resistances of the porous sublayer and of the toplayer, whereas the resistance of the liquid boundary layer is determined by hydrodynamics. In previous papers the influence of this latter important parameter in the pervaporation process has been discussed [18-19]. In this paper the results are discussed concerning the development of a thin selective toplayer. For the preparation of homogeneous membranes different elastomers are used in this chapter and their pervaporation behaviour has been determined. Two model solutes have been used here, trichloroethylene as an example for chlorinated compounds and toluene as a model solute for aromatic compounds.

4.2 PROPERTIES OF ELASTOMERS

4.2.1 Chain mobility

Diffusion rates of penetrants in polymers generally depend on the mobility of the segments in polymer chains. The chain flexibility in elastomers is determined by the presence of steric groups, chain interactions and the polymer back-bone structure.

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For the back-bone structure important effects may stem from:

- type of atoms
- degree of saturation
- presence of aromatic or heterocyclic groups
- cis/trans configurations

C-N-C, C-O-C and Si-O bonds are well known for their high flexibility, whereas aromatic or heterocyclic groups in the chain and unsaturated bonds with trans configurations diminish chain mobility. When double bonds are present in the polymer back-bone two opposing effects are observed with respect to chain mobility. Rotation around the C=C bond is excluded, whereas neighboring C-C bonds have a larger space available compared to fully substituted chains. The net result, however, is a somewhat higher chain mobility [20, 21, 22].

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Side groups determine to a large extent chain interactions and affect the rotation of the main chain. In almost every polymer hydrogen atoms are found as the main substituent. Because of the small dimensions of the hydrogen atom, chains of unbranched hydrocarbons have a relatively high mobility and high packing density. A too regular structure, however, enhances crystallinity, thus decreasing the flexibility of the chains. Both chain mobility and chain interactions are altered, when H-atoms are substituted by other atoms or groups. Chain stiffness is enhanced as a result of steric hindrance which diminishes the rotation of chain segments. Although introduction of large side groups will also lead to an increase in chain distance the net result will be an increase of chain

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stiffness, except in the case of flexible side groups (e.g. alkyl groups), when the chain distance will have a dominating effect.

Physical chain interactions can be subdivided into dipole forces, dispersion forces and hydrogen bonding forces. Dispersion forces are relatively small interactions which are always present between macromolecular chains. Polar interactions (dipole forces) are stronger and can be found in elastomers such as chloroprene rubber. The strongest interactions are hydrogen bonds. These interactions, however, are still relatively small compared to the chemical bonding of individual chains in macromolecules by a cross-linking reaction.

4.2.2 Cross-linking

The terms cross-linking or vulcanization are both used synonymously for chemically tying independent chain molecules into a molecular network. As a result of this vulcanization process a rubber is obtained with improved mechanical and chemical properties. The cross-links in elastomeric networks can have a different nature depending on the vulcanization process chosen. In general cross-linking can be brought about by using the following vulcanizing agents [23]:

- sulfur
- peroxides
- polyvalent organic compounds (phenolic resins, quinone derivatives or maleimides)
- metal oxides.

Furthermore cross-linking also occurs with other techniques, like gamma- and X-ray irradiation or a thermal treatment. As a result the junctions may be single sulfur atoms, chains of sulfur atoms, carbon - carbon bonds, polyvalent organic segments or polyvalent metal ions.

Traditional vulcanization of diene-like elastomers

Traditionally sulfur is used in the cross-linking of elastomers. Vulcanization of the first commercial rubber was accomplished by mixing 8 parts of sulfur per 100 parts of rubber and took typically 5 hours of heat treatment at 140 °C. The addition of activators, like zinc oxide, and the use of accelerators reduced the vulcanization time to as little as 2 to 5 minutes.

In the case of accelerated sulfur vulcanization of elastomers, the sulfur attacks the rubber hydrocarbon almost exclusively at allylic positions. Therefore allylic hydrogen atoms have to be present in the elastomeric molecule. Double bonds are broken and a sulfur bridge between two polymer chains is formed (see fig. 1). The attacking species from the vulcanization system (cross-linking agent and accelerator) must contain sites for proton acceptance and electron acceptance in proper steric relationship to permit rearrangements in the molecules as shown for accelerated sulfur vulcanization.

Several polyvalent organic compounds have such sites too and are used with unsaturated diene-like elastomers in the manufacture of specialty rubbers (see fig. 1). Vulcanization by phenolic resins for example is extensively used with butyl rubber in high temperature applications.

Chloroprene rubbers (CR) are generally cross-linked by the action of metal oxides. The primary cross-linking agent is zinc oxide, which is used along with magnesium oxide (see fig. 1).

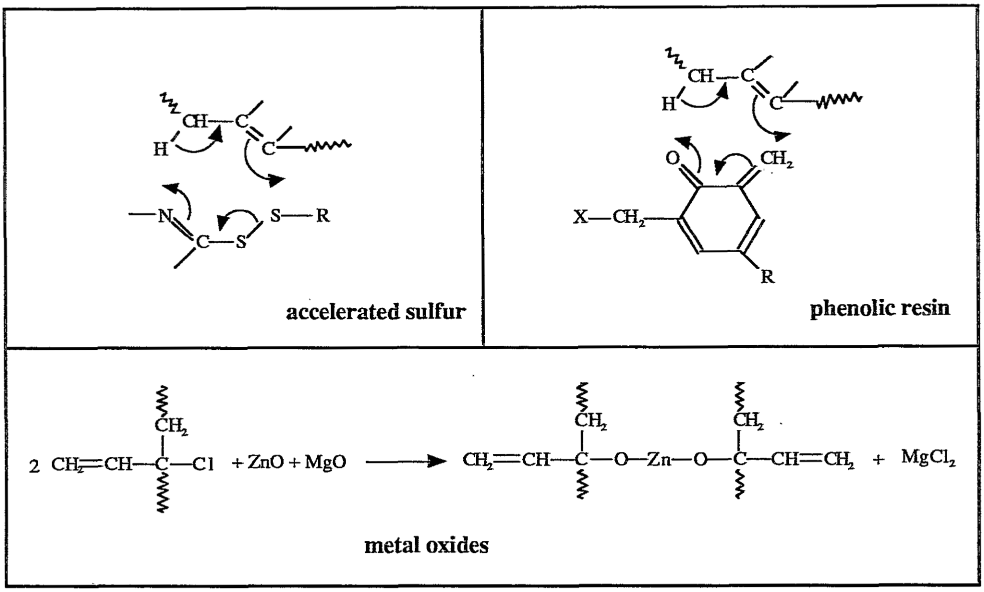


Figure 1: Schemes for some cross-linking procedures of diene-like elastomers

Vulcanization of saturated elastomers

Many newly developed basic elastomeric materials are fully saturated. The absence of allylic hydrogens is often compensated for by copolymerization with an unsaturated diene-like monomer. Alternatively, however, specific cross-linking reactions are developed for fully saturated elastomers.

Silicone rubber can be cross-linked by a Room Temperature Vulcanization (RTV) reaction. In this system cross-linking occurs either through a catalyzed hydroxy condensation [24] or a hydro silylation reaction [25] as indicated in figure 2.

In the condensation reaction a hydroxyl end-blocked polysiloxane is mixed with a polyfunctional organo-silicate which acts as a cross-linking agent, and with a catalyst to promote condensation. This reaction takes place already at room temperature. In this system, the cross-linking agent becomes a part of the network, but, because it is also a silicone, the heat stability is not altered. In RTV-systems the condensation reaction is commonly applied.

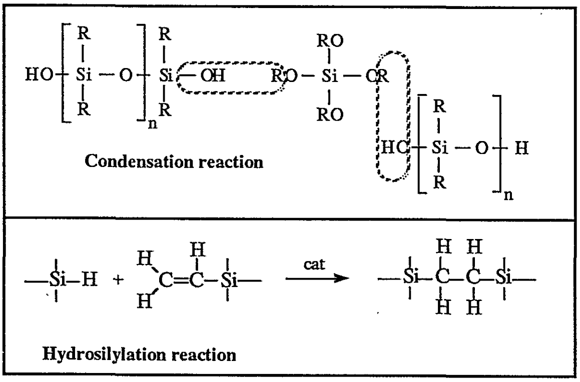


Figure 2: Silicone rubber Room Temperature Vulcanizing (RTV) systems

Peroxides

An alternative way of silicone rubber vulcanization is brought about by a free radical - initiated reaction. Peroxides decompose thermally into two oxy-radicals, which are very reactive and abstract hydrogen atoms from polymer chains. Two polymer radicals then combine to form a cross-link. The peroxides do not incorporate into the polymer network in contrast to the condensation and hydro silylation reaction described above, or the way rubbers are cross-linked by sulfur. This is important in the cross-linking of silicone rubber, because the heat stability is reduced when carbon atoms are introduced between molecules.

Peroxide vulcanization is also useful in the cross-linking of saturated elastomeric molecules, where a sulfur vulcanization is impossible, because of the absence of reactive double bonds. Ostromysslenski discovered already in 1914 [26] the possibility of cross-linking natural rubber with benzoyl peroxide. However, benzoyl peroxide vulcanizates have lower strength and poorer heat resistance than sulfur vulcanizates. With the development of other peroxides in the 1950's and the development of the fully saturated ethylene-propylene copolymers, peroxides became more and more of interest. The basic reactions in a peroxide initiated cross-linking reaction are summarized in figure 3.

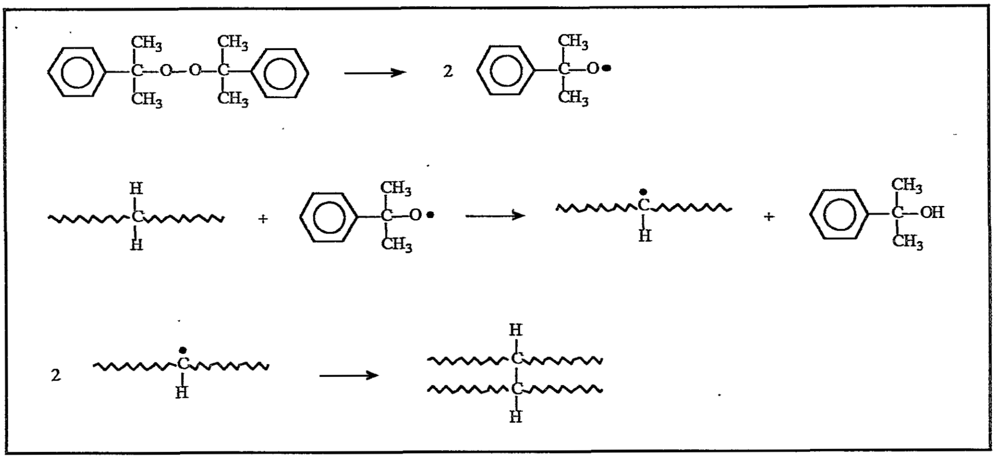


Figure 3: Peroxide vulcanization system

Dicumylperoxide has a broad utilization capability as cross-linking agent, because it combines efficiency and good cross-linking properties with low cost. The decomposition characteristics are such as to yield a rapid cure at 150 °C, whereas the decomposition products are relatively harmless. The non volatility of the cross-linking agent prevents loss during mixing.

Decomposition rates in vulcanization processes are usually given in terms of half-lives. The half-life curves for DCP are given in a Hercules data bulletin [27] and range from 6 to approximately 12 minutes at 155 °C for the elastomers described in this paper. It can be calculated that after 7 to 10 half-lives in any peroxide system a plateau is reached. However, it is not necessary to cross-link such a long time. After 3 to 4 half-lives mechanical properties, like tensile strength, modulus and compression set, have attained about 90 % of their ultimate value. Short curing cycles are often preferred, because of a resulting lower degree of polymer degradation which follows from small amounts of degradation initiating compounds which are always present.

Résumé

For the preparation of elastomeric pervaporation membranes dicumylperoxide is chosen as the general cross-linking agent. The advantages over other cross-linking systems are:

- easy to handle
- broadly applicable
- no incorporation of "foreign" molecules into the network
- low volatility
- acceptable cross-linking temperatures.

4.3 THEORY

4.3.1 Resistance-in-series model

A mass transfer resistance-in-series model was explored elsewhere [18, 19] to describe the mass transfer of the organic component in the pervaporation process. The transport behaviour of the membrane was determined from thickness dependent pervaporation experiments, yielding a membrane mass transfer coefficient, which equals the ratio of the permeability coefficient and the thickness for the investigated homogeneous membranes. A similar approach was followed for composite membranes, only now an effective membrane thickness obtained from permeation measurements was used. Furthermore, the boundary layer mass transfer coefficient at one fixed cross-flow velocity could be obtained from these measurements. The basic equations to determine the effect of the liquid boundary layer in the pervaporation process are given below.

$$J_{oc} = k_{OV} \cdot \phi_{oc}^{b} \tag{1}$$

The overall mass transfer coefficient k_{OV} [m/s], can simply be determined from measurements of bulk feed concentration and steady state permeate component flux in the pervaporation experiments. The reciprocal overall mass transfer coefficient ($1/k_{OV}$), which actually can be considered as an overall mass transfer resistance, consists of two terms:

1) the boundary layer resistance ($1/k_L$) and

2) the membrane resistance ($\frac{1}{k_M} = \frac{\ell}{\mathcal{P}_{oc}}$).

$$\frac{1}{k_{OV}} = \frac{1}{k_L} + \frac{1}{k_M} = \frac{1}{k_L} + \frac{\ell}{\mathcal{P}_{oc}} \tag{2}$$

The overall mass transfer coefficient (k_{OV}) is obtained from pervaporation measurements, whereas the thickness of the investigated membrane can be measured using a digital micrometer. If the cross-flow velocity (and therefore $1/k_L$) is now fixed for all experiments, the membrane permeability can be obtained from equations (1) and (2) as will be described below (section 4.5.2).

The water flux is not altered because of concentration polarization phenomena [18], which makes it possible to calculate the water permeability according to equation (3).

$$\mathcal{P}_w = J_w^p \cdot \ell \qquad (3)$$

It is now also possible to calculate the so called "intrinsic pervaporation selectivity", which is the membrane selectivity in the hypothetical case that boundary layer effects could be excluded.

$$\alpha^i_{oc/w} = \frac{\mathcal{P}_{oc}}{\mathcal{P}_w} \qquad (4)$$

4.3.2 The solubility parameter approach

A semiquantitative way to describe the interactions between polymer and solutes is the solubility parameter theory [28]. This theory was initially developed to explain the mixing behaviour of liquids, but it is also very useful in predicting the compatibility of polymers and solvents.

The process of dissolving a polymer in a solvent is determined by the free energy of mixing:

$$\Delta G_m = \Delta H_m - T\Delta S_m \qquad (5)$$

Since the swelling of a polymer in a solvent is connected with a relatively small increase in entropy, the magnitude of the enthalpy term ΔH_m is an important factor in determining the sign of the free energy change: ΔH_m should be as low as possible. Hildebrand and Scott [29] proposed that:

$$\Delta H_m = V_{mixt} \cdot \left[\left(\frac{\Delta E_i}{V_i}\right)^{1/2} - \left(\frac{\Delta E_j}{V_j}\right)^{1/2}\right]^2 \cdot \phi_i \cdot \phi_j \qquad (6)$$

The expression $(\Delta E_i/V_i)$ is the energy of vaporization per cubic centimeter, which has been often described as the "internal pressure" or the "cohesive energy density" and it is related to the solubility parameter:

$$\delta_i = (\Delta E_i/V_i)^{1/2} \tag{7}$$

The total energy of vaporization can be considered as the sum of energies required to overcome dispersion forces (ΔE_d), polar interactions (ΔE_p) and breaking of hydrogen bonds (ΔE_h) [30].

$$\Delta E_i = \Delta E_d + \Delta E_p + \Delta E_h \tag{8}$$

Combining equations (7) and (8) gives:

$$\delta_i^2 = \delta_{d,i}^2 + \delta_{p,i}^2 + \delta_{h,i}^2 = \delta_{d,i}^2 + \delta_{p/h,i}^2 \tag{9}$$

The heat of mixing is related to the solubility factor and it depends on the value of $(\delta_1 - \delta_2)^2$. If this value approaches zero the heat of mixing will be minimal and the two substances will mix, due to the $T\Delta S_m$ term. For macromolecules the same conditions hold. The polymer and a single penetrant will show good interaction if δ_1 approaches δ_2.

Due to mutual interactions between the components of the liquid feed mixture the solubility parameter approach is usually less succesfull for polymer samples in binary liquid mixtures. Still for certain binary mixtures good correlations have been observed [31, 32]. In the present paper we restrict ourselves to the chemical nature of the elastomer. With respect to this, solubility parameters give an indication of the polarity/hydrophilicity of the membrane material through the combined solubility parameter for polar and hydrogen bonding contributions ($\delta_{p/h}$).

Although extensive tabulations of δ-parameters for liquids are available, data on polymers are limited. Several authors determined solubility parameters on the basis of group contributions [33-35]. Van Krevelen [33] gives the most extensive tabulations and subdivides the overall solubility parameter in contributions due to dispersion, polar and hydrogen bonding forces. A clear advantage of determining the three dimensional parameters in this way is that all values are calculated in the same way and thus errors caused by the use of different experimental methods are excluded.

4.4 EXPERIMENTAL

4.4.1 Materials

The polymers used in this study are listed in table 1 and were kindly supplied by Helvoet BV., Hellevoetsluis, Netherlands.

The solvents (analytical grade) for dissolving the polymers and the cross-linking agent dicumylperoxide (DCP) were purchased from Merck and are used without further purification.

For homogenization of the demixed two-phase permeate we used ethanol of analytical grade which was dried on molecular sieves.

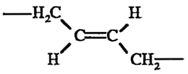
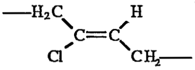
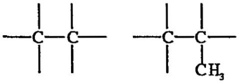
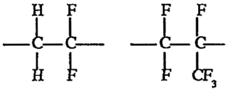
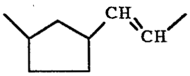
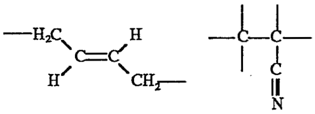
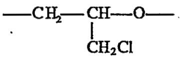
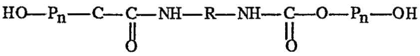
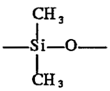
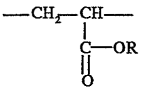
Water was deionized and ultrafiltrated before use.

4.4.2 Membrane preparation

The polymers are dissolved in a suitable solvent and a certain amount of DCP is added. For the preparation of homogeneous membranes the polymer solutions are casted on a clean glass plate and the solvent is evaporated overnight. Polyoctenamer and polybutadiene membranes were casted upon Teflon® plates. The next day the elastomers are crosslinked during 45 minutes at 155 °C. After cooling, the plates are placed in a water bath and after 24 hours the membranes are carefully removed from the plates. The evaporation, cross-linking and cooling step are carried out in a nitrogen atmosphere. The homogeneous membranes obtained in this way have usually a thickness of 80 - 150 μm.

For the preparation of silicone rubber membranes a different procedure is followed. The polymer and cross-linking agent are purchased from General Electric (RTV 615 A + B). The two components are mixed and when the solution is free of air-bubbles the solution is casted on a Perspex® (polymethylmethacrylate) plate. To reduce the time of cross-linking the silicone rubber membranes are cured on the plate at 70 °C overnight in a nitrogen atmosphere. The thickness of the silicone membranes was usually 60 - 80 μm.

Table 1: List of elastomers studied

Elastomer (product name)	**Abbreviation**	**Membrane thickness used [µm]**	**Molecular structure**
Polybutadiene (Finaprene 250)	BR	50 - 150	
Polychloroprene (Neoprene TW)	CR	50	
Ethene - Propene terpolymer (Keltan 578)	EPDM	40 - 200	 $-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}- \quad -\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{CH_3}{C}}-$
Fluorocarbon elastomer (Viton® GF)	FKM	100	 $-\overset{H}{\underset{H}{C}}-\overset{F}{\underset{F}{C}}- \quad -\overset{F}{\underset{F}{C}}-\overset{F}{\underset{CF_3}{C}}-$
Polynorbornene (Norsorex)	PNR	120	
Polyoctenamer (Vestenamer®)	OT	140	$-(CH_2)_3-CH=CH-(CH_2)_3-$
Nitrile Butadiene Rubber (18, 28, 33 en 38% AN) (Perbunan 1807 - 3807)	NBR	120 - 160	
Epichlorohydrin terpolymer (Hydrin 400)	ETER A	180	 $-CH_2-\underset{CH_2Cl}{CH}-O-$ (polyepichlorohydrin)
Polyurethane (Urepan 640)	AU	170	 $HO-P_n-C-\underset{O}{\underset{\Vert}{C}}-NH-R-NH-\underset{O}{\underset{\Vert}{C}}-O-P_n-OH$
Polydimethylsiloxane (General Electric RTV 615)	PDMS	60 - 240	 $-\overset{CH_3}{\underset{CH_3}{Si}}-O-$
Polyacrylate rubber (Hycar® 4051 EP)	ACM	140	 $-CH_2-\underset{\underset{\underset{O}{\Vert}}{C-OR}}{CH}-$

4.4.3 Sorption experiments

Films of polybutadiene, copolymerized with 38 % of acrylonitrile (NBR (38)) were prepared by pouring out a dicumylperoxide (DCP) containing polymer solution in a petri dish. After the solvent has been evaporated the films were cross-linked at 155 °C. The vulcanization times were in the range of 10 - 60 minutes. The petri dishes were cooled and filled with water. After a night of submersion free films with a thickness of approximately 300 µm were obtained.

Before performing sorption experiments strips of NBR(38) were immersed in pure solvent. Depending on the pure liquid used in the sorption experiment, ethanol or toluene was used to remove low molecular weight fractions from the polymer. After one day of submersion the strips were dried in vacuo until no significant weight decrease was observed anymore.

For the sorption experiments strips of NBR(38), with a dry weight of approximately 0.15 g, were immersed in conical flasks containing either ethanol or toluene. After 24 hours of sorption at room temperature, the strips were removed from the liquid, carefully blotted between tissue paper, put in a closed petri dish and weighed.

The sorption of pure solvents is expressed as the solvent weight fraction in the swollen polymer (w_{solv}), which equals the ratio of the solvent uptake (m_{solv}) and the weight of the polymer sample after submersion (m_{tot}):

$$w_{solv} = \frac{m_{solv}}{m_{tot}} \qquad (10)$$

4.4.4 Pervaporation experiments

The pervaporation experiments have been performed with a laboratory pervaporation set-up, as described previously [18]. A 5 liter thermo-regulated storage tank (25 °C) with Viton® feed and recycle lines is connected to a centrifugal pump that allows an average flow rate of approximately 2 l/min. This is large enough to prevent a concentration drop over the four pervaporation cells in series. The feed concentration in the feed tank is kept constant by a continuous supply of the organic component. The pressure at the permeate side was kept below 3 mbar by a vacuum pump.

Steady state conditions were achieved after 3 - 4 days of pervaporation. After the permeate was collected in cold traps (cooled by liquid nitrogen) flux and selectivity were determined, according to the following equation:

Component flux: $$J_i^p = \frac{m}{A\,.\,t} . \frac{w_i^p}{\rho_i} \qquad (11)$$

The concentrations of the aqueous solutions of toluene and trichloroethylene respectively were 250 and 500 µg/g which allows to assume a concentration independent feed density of approximately 1000 kg/m^3.

The actual selectivity $\alpha_{oc/w}$ observed in the pervaporation experiments can be deduced from the compositions in the permeate and the feed solution respectively

$$\alpha_{oc/w} = \frac{(w_{oc}^p / w_w^p)}{(w_{oc}^f / w_w^f)} \qquad (12)$$

4.4.5 T_g-measurements

For determination of the glass transition temperatures of the elastomeric membranes investigated, calorimetric experiments were performed on a Perkin Elmer DSC 4. First the samples (mass ~ 20 mg) were cooled at maximum speed to -130 °C. After equilibrium was reached the heat effects during a controlled heating run at a scanning rate of 10 °C/min were measured.

4.5 RESULTS AND DISCUSSION

4.5.1 Determination of the cross-link time

The influence of the vulcanization time on the sorption characteristics was determined with NBR(38) films in pure liquids at room temperature. Figures 4 and 5 show the weight fraction of solvent in the swollen film, as a function of the vulcanization time and the weight fraction of DCP. Two liquids are used in these experiments; toluene as a strongly swelling agent and ethanol as a moderately swelling agent. The figure for toluene uptake shows that already after 10 minutes (about one half life) of vulcanization, with 0.5 wt% of DCP or more, solvation of the polymer is prevented. For 0.25 wt% DCP prolongation of the cross-link time to 30 minutes is necessary. Longer curing times slightly diminish the degree of swelling, whereas up till 2.0 wt% of DCP the swelling values do decrease with increasing amount of cross-linking agent.

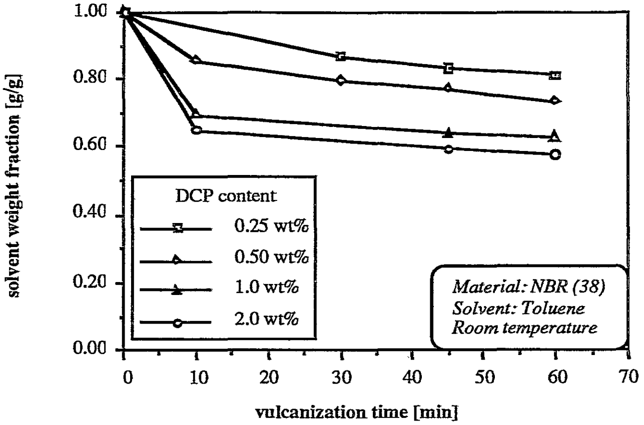


Figure 4: Sorption of toluene as a function of vulcanization time and DCP-content for NBR(38)

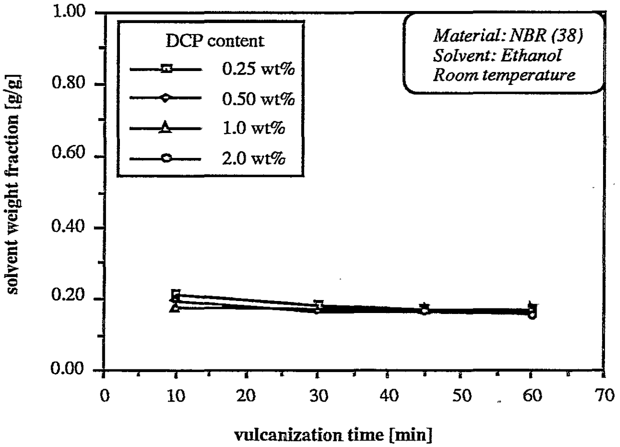


Figure 5: Sorption of ethanol as a function of vulcanization time and DCP-content for NBR(38)

Ethanol is a nonsolvent for NBR(38)-rubber and consequently lower degrees of swelling are observed. Figure 5 shows that at a vulcanization time of 10 minutes, higher amounts of added DCP lead to diminished swelling. After 30 minutes of vulcanization or longer, only minor differences in swelling behaviour are observed and a mean solvent weight fraction of 0.169 ± 0.006 g/g is obtained.

Arbitrarily a vulcanization time of 45 minutes (4 half lives) for all elastomers used in the pervaporation experiments has been chosen. After this time, the swelling of films in moderately swelling agents, like ethanol, has become independent of the vulcanization time or added amount of DCP.

Increasing the vulcanization time with one half life, from 45 to 60 minutes, can reduce the degree of swelling in toluene by another 4 wt%, but short cross-linking times are preferred, to diminish polymer degradation.

4.5.2 Pervaporation performance of various elastomers

The pervaporation experiments have all been performed at a temperature of 25 °C. The thickness of the membranes varied from 40 - 200 μm (see table 1) and the feed compositions chosen were about half of the maximum solubility of the components in water:

- trichloroethylene/water: 500 μg/g (max. solubility: 1100 μg/g [36]);
- toluene/water: 250 μg/g (max. solubility: 500 μg/g [37]).

The permeabilities have been calculated according to equations (1) - (3). The liquid boundary layer mass transfer coefficient required to solve equations (1) and (2) is obtained from a previous research study [18] in which experiments were performed at identical cross-flow conditions and with identical pervaporation cells. In this study composite and homogeneous membranes of PDMS with a very low membrane resistance towards the organic component had been used. From a linear regression fitting procedure boundary layer mass transfer coefficients of $2.5*10^{-5}$ m/s and $2.3*10^{-5}$ m/s were obtained for binary aqueous solutions of toluene and trichloroethylene respectively.

NBR membranes

The pervaporation performance of NBR membranes has been determined to investigate the influence of polar and slightly hydrophilic groups in the membrane material. Figure 6 shows the permeability coefficients for nitrile copolymers of polybutadiene with acrylonitrile contents in the range of 0 - 38 %.

A higher nitrile content decreases the permeability of the organic component. The water permeability, however, seems to be almost independent of the acrylonitrile content. This last observation is in agreement with the work of Salame [38], who studied the transport properties of gases and water vapour in nitrile polymers. The water permeability appeared to be almost independent of the nitrile ratio, unless the ratio exceeded a value of 0.6. The author stated, that an explanation could be found in terms of the solution-diffusion model. The increase in solubility of water due to the introduction of nitrile groups was obviously opposed by a decrease in diffusion. At higher nitrile contents diffusion reduction became dominant and the water permeability dropped. As far as sorption was concerned this explanation was endorsed by the work of Edwards [39], who studied water absorption phenomena in peroxide cured elastomers and actually reported a relatively higher weight increase for copolymers of polybutadiene and acrylonitrile than for the homopolymer polybutadiene. In the case of the organic component, both factors (diffusion and sorption) were expected to act in the same direction and a decrease in permeability and selectivity was obtained with increasing acrylonitrile content.

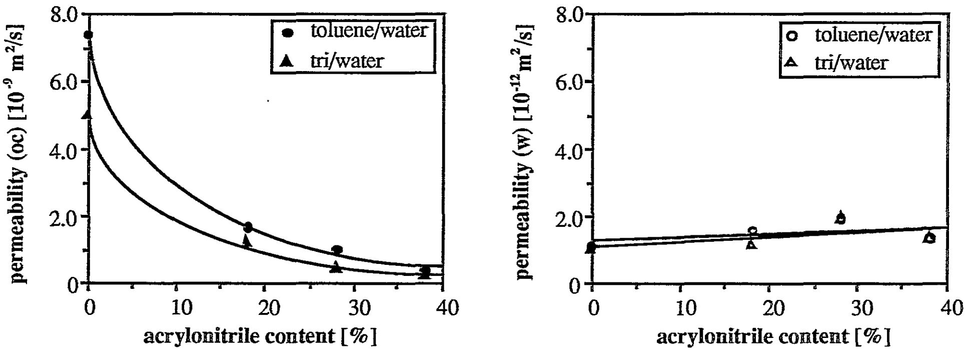


Figure 6: Permeabilities of water, toluene and trichloroethylene in NBR membranes for the pervaporation of binary aqueous solutions

NBR membranes and other copolymers of polybutadiene have also proven to be excellent model polymers in the separation of organic mixtures [40-42]. The permeation rates of the different components from butadiene/isobutene and benzene/n-heptane mixtures decreased with increasing content of acrylonitrile in the rubber. This was caused by a decrease in swelling as well as a decrease of the diffusion rate. Introduction of non-polar groups e.g. in polybutadiene-based copolymers with styrene (SBR) showed, that compared to NBR membranes the sorption behaviour of benzene/n-heptane mixtures was not altered very much going from a low to a high content of styrene in the copolymer. Pervaporation experiments with the same mixture, however, showed a clear dependence on the styrene ratio. From this, one can deduce that diffusion rates of permeants in polybutadiene based membranes were reduced due to the introduction of styrene groups. These observations indicate, that NBR membranes are interesting model elastomers, because the polarity of the membrane can be changed in a very accurate way, so that both the diffusion as well as the sorption in the membrane and thus the pervaporation behaviour are affected.

Other elastomers

The experiments with NBR membranes presented above gave the first quantitative information about the pervaporation performance of elastomeric membranes in the removal of volatile organic components from aqueous solutions. In order to obtain more information about the factors determining the transport of water and organics through elastomeric membranes the pervaporation performance of a wide range of elastomers has been studied. In figures 7 and 8 the actual membrane permeabilities observed in the separation of toluene/water and trichloroethylene/water mixtures are given. From the different scales of the two figures it is apparent that the organic component is transferred much more readily than water. Furthermore the water permeabilities appear to vary over a much wider range.

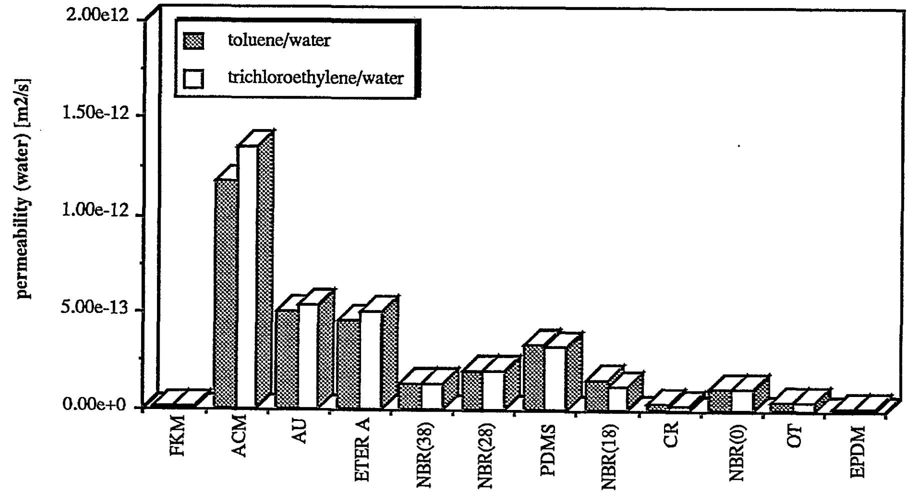


Figure 7: *Actual water permeabilities in the pervaporation of binary aqueous solutions*

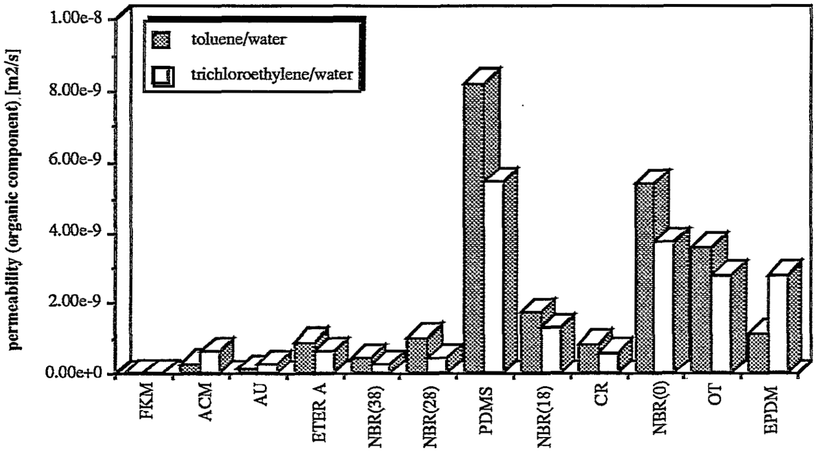


Figure 8: Actual permeabilities for the organic component in the pervaporation of aqueous solutions

Interactions of water with polymers in general and with elastomers in particular have been described and reviewed extensively in literature. Comyn [43] gives the water vapour permeabilities for several elastomers. The values for EPDM, Viton, Neoprene, nitrile rubber and silicone rubber are 0.33 : 0.40 : 0.61 : 4.0 : 14.0 g/m^2-day, respectively. This is in reasonably good agreement with our pervaporation data, where the water permeabilities, schematically represented in figure 7, are 0.92 : 1.1 : 2.5 : 13 : 33 * 10^{-14} m^2/s respectively.

The structural characteristics of elastomers as discussed in a previous section, are often used to predict and explain permeabilities of elastomers. Iyengar [44] tried to correlate quantitatively the water vapor permeability of non-polar elastomers to the presence of steric side groups and degree of unsaturation. The presence of steric groups in butyl rubber and ethylene-propylene rubbers are in this sense responsible for the low water permeabilities mentioned above, whereas a high degree of unsaturation as in polybutadiene enhances water permeability. These statements are confirmed, if the water permeabilities of polybutadiene (BR) and polyoctenamer (OT) are compared. These two elastomers have an almost similar structure. The higher degree of unsaturation in BR would in this sense account for the higher water permeability coefficient.

In general there is an analogy between the diffusion rates of water and the organic molecules in the rubber matrix: if the diffusion coefficient for water in a certain membrane is large, the diffusion coefficient of the organic component will be large too. For membranes that exhibit a comparable sorption behaviour for the organic component, the organic component fluxes will be directly related to the diffusion rates in the membrane. The molecular structures of polybutadiene and polyoctenamer seem to be the most favorable ones to allow high diffusion rates, because they possess unsaturated carbon-carbon bonds, they lack any steric groups, while polar groups are absent. Figure 8 shows that good toluene and trichloroethylene permeabilities are indeed observed for these elastomers.

Again the excellent permeability of polydimethylsiloxane for the organic component is striking and comparable in value with those for completely non-polar hydrophobic elastomers. As stated above in the case of the water permeability, these high permeabilities of PDMS can be ascribed to the extremely high chain mobility in this rubber, resulting in high diffusion rates. Reduction in chain mobility and perhaps lower affinity for the organic component are probably responsible for the low organic component fluxes observed for the other relatively polar/hydrophilic elastomers.

Correlation with structural parameters

The kinds of considerations given above are, however, very dangerous and highly speculative. Differences in the permeation behaviour of the apolar membranes for example tend to be completely ascribed to differences in the transport rates (chain mobility), whereas sorption effects are neglected. As a first attempt to relate the pervaporation performance to structural parameters of the membrane material in a more quantitative way, the permeabilities are correlated to solubility parameters (sorption) as well as to glass transition temperatures (mobility).

The T_g-values determined according to the standard procedure are given in table 2. The high mobility of the silicone rubber chains is expressed by the extremely low T_g-value of -123 °C. Low T_g-values are also obtained for the elastomers without bulky substituents and with a certain degree of unsaturation, e.g. polybutadiene and polyoctenamer. The effect of the rate of unsaturation is clearly shown by the latter two elastomers, which have an almost similar structure (see table 1). The only structural difference is the presence of one double bond on eight carbon atoms in OT, whereas BR contains one double bonds after every fourth carbon atom. In the range of NBR membranes the position of the glass transition point shifts to higher temperatures when the acrylonitrile content is increased.

In figure 9 the permeabilities of the components of the binary liquid mixture are given as a function of the glass transition temperature. Where so many other factors are often believed to be of importance with respect to permeability coefficients, it is rather surprising to see the dominant effect of the T_g-value on the permeability of the organic component in figure 9. The permeability for the organic component drastically increases with decreasing glass transition temperature. An important observation with respect to the good correlation found for the glass-transition temperature and the permeability coefficient of the organic component, which has been discussed previously [18], is the non-coupled transport of water and the organic component in the elastomeric pervaporation membranes. This observation should be kept in mind for all the data presented in figures 9 and 10.

elastomer	T_g [°C]
BR	- 91
CR	- 40
EPDM	- 46
FKM	- 9
OT	- 77
NBR(18)	- 49
NBR(28)	- 35
NBR(38)	- 26
ETER A	- 44
AU	- 23
PDMS	- 123
ACM	- 17

Table 2: Glass transition temperatures for the elastomeric membranes studied

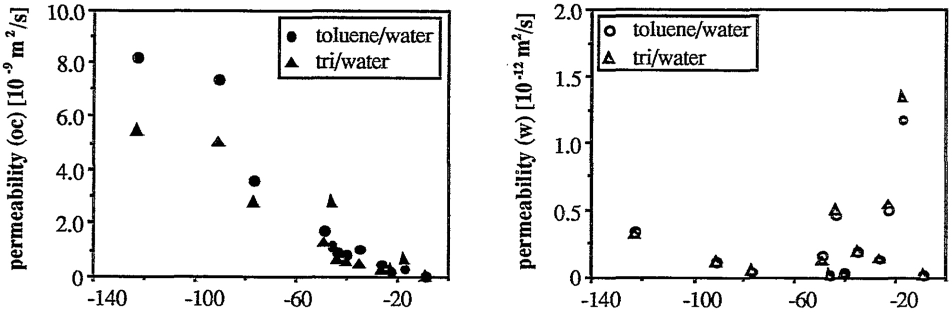


Figure 9: Dependence of the permeabilities for the organic component (left) and for water (right) on the glass transition temperature

The water permeabilities only increase with decreasing glass transition temperature for elastomers with a T_g smaller than -60 °C (PDMS, BR, OT). At higher T_g's no clear information can be obtained due to a lot of scattering, but in several cases very high water fluxes are observed. The strong hydrogen bonding ability in relatively polar and hydrophilic elastomers (AU, ETER A, ACM) is probably responsible for these observed high water fluxes.

The polarity/hydrogen bonding capacity of the elastomers is expressed through the combined solubility parameter for polar and hydrogen bonding contributions ($\delta_{p/h}$). This parameter is used to correlate qualitatively membrane permeabilities with the chemical nature of the elastomer. The contributions to the three dimensional solubility parameters of the elastomers are given in table 3 both calculated from group contributions [33] and taken from literature [28, 30, 45].

Table 3: Solubility parameters of various elastomers and penetrants

		ρ	δ_d		δ_p		δ_h		$\delta_{p,h}$	
no	ELASTOMER	[g/cm^3]	calc	lit.	calc	lit.	calc	lit.	calc	lit.
1	Polybutadiene	0.89	15.5	17.5	0	2.3	0	3.4	0	4.1
2	Nitrile-Butadiene Rubber (18 % AN)	0.93	15.7	18.3	4.3	5.6	2.8	3.7	5.1	6.7
3	Nitrile-Butadiene Rubber (28 % AN)	0.95	15.5	18.7	6.9	7.4	3.5	3.9	7.7	8.4
4	Nitrile-Butadiene Rubber (38 % AN)	0.97	16.0	19.1	9.7	9.2	4.2	4.1	10.6	10.1
5	Polychloroprene	1.21	16.0	19.4	7.7	3.1	2.4	2.7	8.1	4.1
6	Epichlorohydrin terpolymer	1.33	16.8	18.6	9.8	8.2	7.0	7.2	12.0	10.9
7	Acrylate rubber	1.15	16.5		5.7		9.0		10.7	
8	Polyoctenamer	0.87	16.0		0		0		0	
9	Ethene-propene terpolymer	0.85	16.0	18.0	0	0.8	0	2.1	0	2.2
10	Polydimethyl siloxane	0.97	-	16.0	-	0.1	-	4.7	-	4.7
11	Polyurethane	1.15	16.9	17.4	5.6	5.1	9.0	10.2	10.6	11.4
12	Fluorinated elastomer	1.69	14.0	15.3	7.8	7.2	0	5.3	7.8	8.9
	PERMEANT									
	toluene	0.87		18.0		1.4		2.0		
	trichloroethylene	1.46		18.0		3.1		5.3		
	water	1.00		19.5		17.8		17.6		

In the case of polyurethane, poly acrylate rubber and the fluorocarbon elastomer the exact chemical structure of the polymer is unknown. For polyurethane in table 3 the parameters for polytetramethylene glycol adipate, are taken as representative. The solubility parameters for the acrylate rubber are based on values for polyethylacrylate. A 70/30 copolymer of polyvinylidenefluoride and polyhexafluoropropylene is used in the calculation of the solubility parameters for the fluorinated rubber. The calculated values are compared to data found in literature. In general there is a good agreement between literature and calculated values. The calculated value for the "polar solubility parameter" of polychloroprene, however, is probably too high [28], whereas in literature deviating values have been reported for the "hydrogen bonding parameter" of fluorinated elastomers [28].

The role of polar interactions and the hydrogen bonding ability ($\delta_{p/h}$) on the water permeability in pervaporation is illustrated in figure 10. The highest water permeabilities are indeed observed for the relatively polar/hydrophilic membranes, whereas extremely low water permeabilities are observed for the completely apolar/hydrophobic membranes. In the intermediate range no clear information can be obtained from the solubility parameter approach due to scattering results.

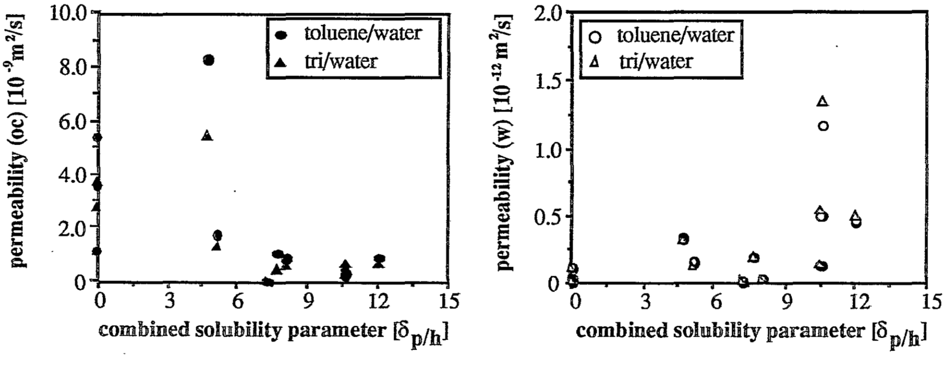


Figure 10: Permeabilities of water (left) and of the organic component (right) for several elastomers in pervaporation using binary aqueous solutions vs. the combined solubility parameter for polar and hydrogen bonding contributions

The polarity/hydrophilicity of the membrane seems to be of only limited importance with respect to the permeability coefficient of the organic component as illustrated in figure 10. The highest permeabilities are observed for PDMS with a value for the combined solubility parameter of 4.6. It can only be concluded that at relatively high values of the combined solubility parameter the permeabilities of the elastomeric membranes for the organic components investigated are low.

For completely apolar/hydrophobic membranes high permeabilities may be observed, but the $\delta_{p/h}$-parameter is not an unequivocal predictor for this variable.

The highest toluene and trichloroethylene permeabilities are observed for non-polar hydrophobic elastomers with a low amount of steric groups and some degree of unsaturation. However, the water permeabilities for these apolar/hydrophobic membranes also increase with decreasing glass transition temperature. For elastomers with a relatively high polarity/hydrophilicity the reduced chain mobility is opposed by a dominating sorption effect. Although some of these observations are confirmed by literature data, especially with respect to water permeabilities, more fundamental research is required to do a firm-based statement on the importance of the two most important factors in the pervaporation process. Therefore the solubility of binary aqueous solutions of trichloroethylene and toluene in elastomeric membranes has been investigated by us [46].

Selection of membrane material

For the development of a thin film composite membrane a proper choice of the elastomeric toplayer is essential. Of course fluxes for the organic component are important; however, they can be improved by decreasing the thickness of the actual separating layer. Effective thicknesses as thin as ~ 1μm can easily be reached. A second and more important criterium for the selection of a suitable polymeric material is selectivity. The intrinsic membrane selectivities, based on the ratio of the pure component permeabilities, for the elastomers investigated are shown in figure 11.

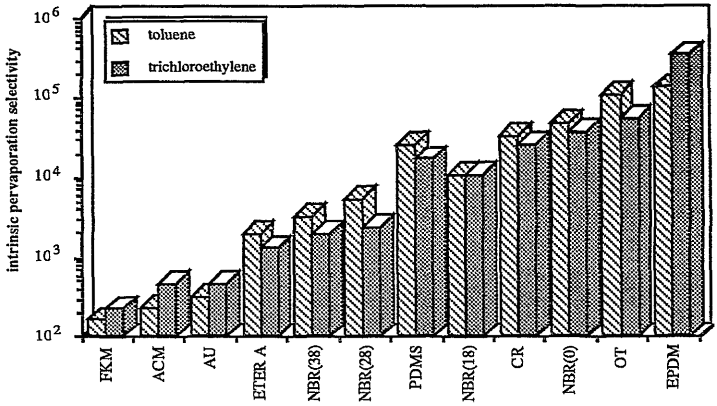


Figure 11: Intrinsic selectivities of elastomeric membranes in the pervaporation of aqueous solutions of toluene and trichloroethylene

In some cases extremely high selectivities are established. This is not caused by an increase in permeability of the organic component, but rather by a very low water permeability. If water fluxes for 100 µm thick membranes are calculated from the permeability data, values of 12 g/m^2-hr for PDMS membranes and 4 - 7 g/m^2-hr for the NBR-membranes are obtained, whereas for EPDM-membranes the water flux is about 0.3 g/m^2-hr. As a result the differences in selectivities between these elastomers become very large (over two orders of magnitude), because the permeabilities of the organic component differ to a minor extent compared to the water permeabilities (see figure 7 and 8).

The role of boundary layer effects is illustrated in figure 12 in which the actual selectivities observed in the pervaporation process are given vs. the intrinsic membrane selectivities calculated according to equation (4).

From figure 12 it becomes clear that for low values of the selectivity the intrinsic and the actual pervaporation selectivities differ only marginally. At higher selectivity values the actual selectivity in the pervaporation process starts to deviate from the intrinsic values, due to boundary layer effects. The largest deviation, however, is still smaller than a factor of 5. This illustrates that although organic component fluxes are strongly affected by boundary layer effects, selectivities remain rather unaffected due to the large effect of the water permeability on the intrinsic selectivity.

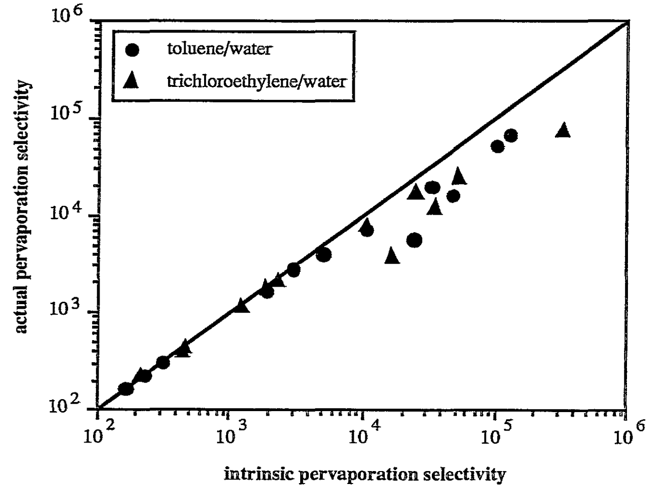


Figure 12: Actual selectivities observed in the pervaporation process vs. intrinsic selectivities of elastomeric membranes in the pervaporation of aqueous solutions of toluene and trichloroethylene

4.6 CONCLUSIONS

Actual membrane permeabilities are obtained from pervaporation measurements on aqueous solutions with small concentrations of volatile organic components. To ensure the correct calculation procedure for the permeabilities the hydrodynamic conditions are taken identical while pervaporation cells with a known value for the liquid boundary layer mass transfer coefficient are used. A wide range of selectivities is obtained for the large variety of elastomers investigated. For this particular application extremely high selectivities (upto 100,000) are established.

The data for the membrane permeabilities can qualitatively be explained in terms of the solution diffusion model. Differences in the permeability of the organic component can be attributed mainly to the physical parameters of the polymer chains. The lower the glass transition temperature (and the higher the chain flexibility) the larger is the transport rate. For the strictly hydrophobic/apolar membranes the same holds for the water permeabilities. The expected high water solubility, when hydrophilic/polar groups are present, can explain the high water permeabilities for these elastomers, although chain mobility due to polar and hydrogen bonding interactions between the polymer chains will be reduced.

For the selection of a suitable membrane material, choosing the elastomer with the highest permeability for the organic component is not obvious, because organic component fluxes are strongly affected by boundary layer effects while water fluxes are not. Choosing the membrane material with a high selectivity and still a good permeability for the organic component will therefore be more profitable.

4.7 LIST OF SYMBOLS

A = membrane area [m^2]
E = energy of vaporization [J/mole]
G_m = free energy of mixing [J/mole]
H_m = free enthalpy of mixing [J/mole]
J = pervaporation flux [m^3/(m^2.s)]
k = mass transfer coefficient [m/s]
ℓ = membrane thickness [m]
m = weight of permeate [kg]

$\mathcal{m}$ = mass [g]
$\mathcal{P}$ = permeability [m^2/s]
S_m = free entropy of mixing [J/(mole.K)]
t = permeation time [s]
T = temperature [K]
V = molar volume [cm^3/mole]
w = weight fraction [g/g]
$\mathcal{w}$ = weight fraction [g/g]

Greek symbols
α = selectivity [-]
δ = solubility parameter [$J^{1/2}/cm^{3/2}$]
ϕ = volume fraction [m^3/m^3]
ρ = liquid density [kg/m^3]

Subscripts
d = dispersion
h = hydrogen bonding
i = component i
j = component j
L = liquid
M = membrane
mixt = mixture
oc = organic component
OV = overall
p = polar
solv = solvent
w = water
tot = total
1 = component 1
2 = component 2

Superscripts
b = bulk
f = feed
i = intrinsic
p = permeate

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CHAPTER 5

SELECTIVE SORPTION FROM AQUEOUS SOLUTIONS IN ELASTOMERS

H.H. Nijhuis, M.H.V. Mulder and C.A. Smolders

SUMMARY

The sorption behaviour of elastomeric membranes in aqueous solutions of toluene and trichloroethylene is studied. The sorption and selective transport of water and organic component are related to the chemical nature of the membrane by the solubility parameter approach. A satisfactory correlation for the sorption of water with the solubility parameter for polar and hydrogen bonding contributions ($\delta_{p/h}$) *is obtained. The solubility of the organic component appears to be independent of this combined solubility parameter.*

Flory-Huggins thermodynamics is applied to describe and predict the sorption behaviour of pervaporation membranes in a more quantitative way. Polymer/liquid interaction parameters and the molecular weight between cross-links are obtained from swelling experiments in pure liquids, whereas the liquid/liquid interaction parameter is calculated from the simple binary Flory-Huggins equations and the solubility of the organic component in water. The characteristic data thus obtained are used in ternary Flory-Huggins equations to describe with reasonable good accuracy the sorption behaviour of the aqueous solutions.

Experimental sorption isotherms for acrylonitrile containing copolymers of polybutadiene, as well as for polydimethylsiloxane and a terpolymer of ethylene-propylene rubber, show that a "Henry-type" of sorption behaviour of the organic component may be assumed in the low concentration range. This direct proportionality between the volume fraction of the organic component in the swollen film and the feed concentration is also predicted by the ternary Flory-Huggins equations.

5.1 INTRODUCTION

In the last three decades much research has been performed to understand the solubility and diffusivity of permeants in polymer membranes. The most commonly used model to describe the transport through dense homogeneous membranes, is the solution-diffusion model [1]. The performance of dense homogeneous membranes is strongly affected by the solubility of the permeating components in the polymer matrix. Prediction of solubility requires a reliable theoretical equation, for which Flory-Huggins thermodynamics [2,3] can be applied.

The simple Flory-Huggins equation holds only for amorphous polymers. In semi-crystalline or crosslinked network structures the solvent up-take is restricted by the resulting strain in the amorphous polymer chains. Flory and Rehner [4-6] introduced an entropy term for elastic deformation of the polymer chains in a network structure.

The main parameters in the Flory-Huggins and the Flory-Rehner equations that have to be determined experimentally are the binary interaction parameter χ and the average molecular weight between crosslinks M_C. Different procedures have been followed to obtain these parameters for elastomers.

- Doty and Zable [7] determined M_C for a crosslinked polymer from its swelling volume in a solvent for which the value of χ was determined from osmotic pressure measurements with the non-crosslinked form.

- Polymer-solvent interaction parameters have been related to solubility parameters by respectively Scott and Magat [8] and Fedors [9]. The value of χ is obtained from a relation in which the solubility parameter difference is included, whereas the crosslink density is obtained using the original Flory-Rehner equation [5].

- Mullins [10] obtained a value for the molecular weight of a unit from stress-strain measurements and used it to determine the interaction parameter of n-decane in natural rubber. The degree of crosslinking was determined chemically by an infrared spectrometric method by Moore and Watson [11]. The thus obtained value was compared with a value obtained from swelling experiments using a previously [10] determined interaction parameter. A large divergence between the two methods has been observed, which was attributed to a relatively high degree of physical crosslinking.

- Values of the Flory-Huggins solvent-polymer interaction parameter have been evaluated by Bhatnagar [12,13]. Assuming an inverse proportionality of the added amount of the crosslinking agent dicumylperoxide (DCP) and the molecular weight between crosslinks, the experimental parameters χ and M_C could be evaluated.

- Frensdorff [14] investigated the vapour sorption behaviour of non-crosslinked ethylene-propylene elastomers and used a simplified Flory-Huggins equation to estimate the interaction parameters from activity (vapour pressure) dependent measurements.

Interaction parameters determined in either one of the ways given above, can now in principle be used to determine the degree of crosslinking in a test sample of the same elastomer from a swelling experiment using the same solvent. By substitution of the average molecular weight between crosslinks in the Flory-Rehner equation the polymer-solvent interaction parameter can be obtained for pure solvents when swelling experiments are carried out with the same elastomer. For prediction of swelling values in binary aqueous mixtures both parameters (χ and M_C) have to be known.

The objective of this paper is to explore the solubility part in the transport of permeants through membranes. The preferential sorption behaviour of various investigated membranes is qualitatively described through the solubility parameter approach. Another approach, based on Flory-Huggins thermodynamics is presented that describes the solubility of the organic component and water in the membrane in a quantitative way. Binary Flory-Huggins parameters for solute-water, solute-polymer and water-polymer interactions will be evaluated using literature values. The molecular weight between crosslinks (M_C) can be determined then from one single sorption experiment in the pure solvent. When such data are not available, interaction parameters have been determined from swelling experiments using elastomeric films with different crosslink densities. In our opinion this is the most reliable method, because the degree of crosslinking and the interaction parameters needed to describe the preferential sorption from aqueous solutions, are then determined from actual sorption experiments.

Sorption experiments at room temperature have been performed for aqueous solutions of toluene and trichloroethylene respectively. The experimentally determined sorption isotherms will be compared with calculated curves using binary interaction parameters in ternary Flory-Huggins equations.

5.2 THEORY

A mass transfer resistance-in-series model to determine the permeabilities of the organic component in the membrane has been described and used elsewhere [15, 16]. According to the solution-diffusion model the permeability part ($\mathcal{P}$) can be split into contributions due to solubility (S) and diffusivity ($\mathcal{D}$) in the membrane. In the following section it will be shown how these three parameters are related. With respect to the solubility of the components in the membrane the solubility parameter theory can give a first estimation. Flory-Huggins thermodynamics describes the relation between the activity in the membrane and the composition of the swollen film in quantitative terms.

Both the solubility parameter approach and the more quantitative theory of Flory and Huggins will be discussed briefly now.

5.2.1 The solution-diffusion model

The transport through membranes is in first approximation very conveniently described by Fick's law. In 1885 Fick already stated, that in isotropic systems the rate of transfer of diffusing matter through a unit area of a section is proportional (through a Fickian diffusion coefficient) with the concentration gradient (dC_i/dx) measured normal to that section:

$$J_i = - \mathcal{D}_i^F \frac{dC_i}{dx} \tag{1}$$

According to the original solution-diffusion model [1,17,18], however, the flux of a component i through a membrane is proportional (through a thermodynamic diffusion coefficient) with the gradient in chemical potential ($d\mu_i / dx$). In pervaporation in which the pressure difference over the membrane is usually relatively small the flux for component i can be described as follows:

$$J_i = - \phi_i \mathcal{D}_i^T \frac{d \ln a_i}{dx} \tag{2}$$

From equation (2) it becomes clear that the transport rates are determined by two factors:

1) the thermodynamic diffusion coefficient of a component in a membrane;
2) the activity (concentration) of the permeants in the membrane as a function of the distance from the membrane/liquid interface.

Fick's law now can be considered as a special case of equation (2). By substituting $a_i = \gamma_i \cdot \phi_i$ and for constant activity coefficients γ_i ($d\gamma_i / dx = 0$) equation (2) converts into the volumetric form of Fick's Law:

$$J_i = - \mathcal{D}_i^m \cdot \frac{d\phi_i^m}{dx} \tag{3}$$

The concentrations of the organic component in the feed and in the membrane at the membrane/feed interface are related by a dimensionless partition coefficient:

$$S_{M/L} = \phi_1^m / \phi_1^w \qquad (4)$$

Substitution of equation (4) into (3) yields equation (5):

$$J_i = - \mathcal{D}_i^m \cdot S_{M/L} \cdot \frac{d\phi_i^w}{dx} \qquad (5)$$

Usually a direct conversion from activities to volume fractions (or mole fractions) is only valid for ideal mixtures in which $\gamma \sim 1$. The high dilution of the binary liquid feed mixtures used in studies on the removal of trace organics from water by pervaporation justifies a similar conversion over the entire solubility range [19, 20]. This can easily be seen from equations which are commonly applied to describe the concentration dependence of activity coefficients, e.g. the van Laar equation or the Margules equations. These equations show furthermore that the activity coefficient, as a first rough approximation, can be taken to be equal to the reciprocal value of the solubility. If no adequate experimental data are available this approximation is often very useful to obtain a value for this parameter.

$$\gamma_i = \gamma_i^{\infty} = \frac{1}{\phi_i^{sat}} \qquad (6)$$

The product of diffusivity ($\mathcal{D}$) and solubility (S) is called the permeability ($\mathcal{P}$):

$$\mathcal{P}_i^m = \mathcal{D}_i^m \cdot S_{M/L} \qquad (7)$$

Substitution of this new parameter in equation (6) yields a very convenient equation for the transport in the membrane:

$$J_i = - \mathcal{P}_i^m \cdot \frac{d\phi_i^w}{dx} \qquad (8)$$

The steady state component flux J_i can be determined from pervaporation measurements, whereas the concentration in the feed solution is often a known variable provided that boundary layer effects are excluded. However, if concentration polarization phenomena are of importance, additional equations are required to describe the transport in the boundary layer.

It is evident from equation (8) that the permeability coefficient is a lump parameter, which can be very convenient for describing the transport in the membrane. For a more fundamental understanding of the permeation process knowledge is required of the diffusion coefficient and the solubility of the components in the membrane. When the permeabilities are known from pervaporation measurements, such information can in principle be obtained by determining the values of either the partition coefficient or the diffusion coefficient in the membrane. In our case the partition coefficient has been determined, whereas data on diffusion coefficients have been obtained from the ratio of experimental permeability and partition coefficients.

5.2.2 The solubility parameter approach

A semiquantitative way to describe the interactions between polymer and solutes is the solubility parameter theory [21-23]. A brief outline of this theory is given in a previous paper, in which experimental permeability coefficients were related to solubility parameters [16]. The basic idea is that a polymer and a single penetrant will show favourable interaction if $(\delta_1-\delta_2)^2$ is minimal. The solubility parameter δ_i contains contributions from dispersion, polar and hydrogen bonding character, as given by:

$$\delta_i^2 = \delta_{d,i}^2 + \delta_{p,i}^2 + \delta_{h,i}^2 = \delta_{d,i}^2 + \delta_{p/h,i}^2 \qquad (9)$$

Although initially developed to explain the mixing behaviour of liquids, the solubility parameter approach appears to be very useful also in predicting the compatibility of polymers and solvents. Extensive tabulations of δ-parameters for liquids are available. However, literature data for polymers are scarce. Several authors determined contributions of molecular groups to the solubility parameter on the basis of experimental data [24-26]. Van Krevelen [24] gives the most extensive tabulations and subdivides the overall group contribution in contributions due to dispersion, polar and hydrogen bonding forces. A clear advantage of determining the three dimensional parameters in this way, is that all values are calculated in a similar way and thus errors caused by the use of different experimental methods are excluded. Again it should be emphasized that the solubility parameter theory can only predict polymer-penetrant interactions very qualitatively. The sorption behaviour of homogeneous elastomeric membranes can be described in a more fundamental and quantitative way by Flory-Huggins thermodynamics.

5.2.3 Flory-Huggins thermodynamics

Mulder et al. [27] showed that Flory-Huggins thermodynamics is very helpful in predicting concentration profiles and describing the sorption selectivity of cellulose acetate membranes in the separation of ethanol/water mixtures. Bitter [28] developed a modified Flory-Huggins equation for describing the sorption behaviour of polyethylene, polypropylene and natural rubber.

For a binary system the activities are given by [29]:

$$\ln a_i = \ln \phi_i + \left(1 - \frac{V_i}{V_j}\right) . \ \phi_j + \chi_{ij} \cdot \phi_j^2 \qquad (10)$$

$$\ln a_j = \ln \phi_j + \left(1 - \frac{V_j}{V_i}\right) . \ \phi_i + \chi_{ij} \cdot \frac{V_j}{V_i} \cdot \phi_i^2 \qquad (11)$$

χ_{ij} is a binary interaction parameter for components 1 and 2 and is called the Flory-Huggins interaction parameter. Equations (10) and (11) can only be applied for liquid mixtures or non cross-linked high molecular weight polymeric systems. For cross-linked polymers a term describing the energy change due to elastic strain has to be added to equation (11) and at swelling equilibrium the following equation is obtained:

$$\ln \phi_i + \phi_j + \chi_{ij} \cdot \phi_j^2 + \frac{V_i \cdot \rho_j}{M_c} \left(1 - 2M_c / M\right) \left(\phi_j^{1/3} - \frac{1}{2} \cdot \phi_j\right) = 0 \qquad (12)$$

where M_c is the molecular weight per cross-linked unit and M is the molecular weight before cross-linking. The factor (1 - 2 M_c/M) expresses the correction for network imperfections resulting from chain ends. For a perfect network (M = ∞) it reduces to unity. The subscripts i and j refer to the penetrant and the polymer respectively.

For ternary systems, a polymer and a binary liquid mixture, the activities as given by Flory [29] of the organic component (1) and water (2) in the polymer (3) can easily be extended with a cross-linking term as given in the equations (13) and (14).

$$\ln a_1 = \ln \phi_1 + (1 - \phi_1) - \phi_2 \cdot \frac{V_1}{V_2} - \phi_3 \cdot \frac{V_1}{V_3} + (\chi_{12} \cdot \phi_2 + \chi_{13} \cdot \phi_3) \cdot (\phi_2 + \phi_3) - \chi_{23} \cdot \frac{V_1}{V_2} \cdot \phi_2 \cdot \phi_3 + \frac{V_1 \cdot \rho_3}{M_c} (1 - 2M_c/M) (\phi_3^{1/3} - \frac{1}{2} \cdot \phi_3) \tag{13}$$

$$\ln a_2 = \ln \phi_2 + (1 - \phi_2) - \phi_1 \cdot \frac{V_2}{V_1} - \phi_3 \cdot \frac{V_2}{V_3} + (\chi_{12} \cdot \phi_1 \cdot \frac{V_2}{V_1} + \chi_{23} \cdot \phi_3) \cdot (\phi_1 + \phi_3) - \chi_{13} \cdot \frac{V_2}{V_1} \cdot \phi_1 \cdot \phi_3 + \frac{V_2 \cdot \rho_3}{M_c} (1 - 2M_c/M) (\phi_3^{1/3} - \frac{1}{2} \cdot \phi_3) \tag{14}$$

In principle these equations can be substituted in equation (2) giving a general equation for the transport of permeants in the membrane. In this particular application, however, some simplifications can be made. First the molar volume of the polymer is much larger than the molar volumes of the penetrants. Therefore the fourth term on the right hand side of equations (13) and (14) may be neglected. The last term on the right hand side of these equations, which accounts for the effects of crosslinking, has only a second order effect in the systems investigated in which the swelling is low and can therefore probably be neglected. In the case of pure liquid sorption (ϕ_1=0 or ϕ_2=0) equations (13) and (14) reduce to the Flory-Huggins equations for binary systems.

5.2.4 Evaluation of the binary interaction parameters

In first approximation the three interaction parameters χ_{ij} in equations (13) and (14) are considered to be concentration independent. The polymer interaction parameters χ_{13} and χ_{23} can be obtained from swelling data of the polymer in the pure liquids using equation (12) for cross-linked polymers. The liquid/liquid interaction parameter can be obtained from equation (10). To solve this equation a value is required for the activity coefficient of the organic component in the aqueous solution. If experimental data are not available a first rough estimation of the activity coefficient, used to calculate χ_{12}, may be obtained from equation (6) ($a_1 = \gamma_1 \cdot \phi_1 = \phi_1/\phi_1^{sat}$), for which one needs solubility data.

Once the binary interaction parameters are determined, an iteration procedure is used to determine the volume fractions (ϕ_1,ϕ_2 and ϕ_3) in the swollen polymer film as a function of the concentration in the binary liquid mixture. The activity of water is assumed to be unity. The value for the activity coefficient of the organic component in the ternary system in equilibrium, as a first rough approximation was obtained from equation (6). Actual ternary sorption experiments, using a polymer test sample with known binary interaction parameters and molecular weight, should provide a more accurate value, which is used in all the model calculations.

5.3 EXPERIMENTAL

5.3.1 Materials

A list of polymers used in the sorption experiments, their tradenames and molecular structures is given elsewhere [16]. Two elastomers have been selected for extensive investigations on the basis of their pervaporation behaviour [30], whereas a group of copolymers has been selected to vary the polarity and hydrophobicity of the membrane. Polydimethylsiloxane (PDMS; RTV 615 A) and crosslinking agent (RTV 615 B), ethylene propylene rubber (EPDM), polybutadiene (BR) and copolymers of polybutadiene containing 18, 28 and 38% of acrylonitrile (NBR(18), NBR(28), NBR(38)) respectively have been used for the preparation of polymer films.

The solvents (analytical grade) in the sorption experiments and for dissolving the polymers as well as the crosslinking agent dicumylperoxide (DCP) are purchased from Merck. The above polymers and chemicals were used without further purification.

Water for the sorption experiments is deionized and ultrafiltrated before use.

5.3.2 Preparation of polymeric films

Relatively thick homogeneous polymeric films with thicknesses over 300 μm were prepared by filling a petri dish with a solution of the elastomer and a certain amount of the cross-linking agent DCP. After complete evaporation of the solvent the polymer is cross-linked for 45 minutes at 155 °C in a nitrogen atmosphere. After cooling, the petri dishes were placed in a water bath and after 24 hours the free films could be removed.

PDMS films have been prepared by mixing the two components thoroughly without adding any solvent, then pouring the viscous solution in a petri dish, degassing, and cross-linking at 70 °C overnight in a nitrogen atmosphere.

5.3.3 Sorption experiments

Preferential sorption

Dried strips of the elastomers (about 0.2 g) were immersed in conical flasks containing an aqueous solution of toluene or trichloroethylene. As a standard procedure the films were removed after 24 hours of submersion at room temperature, carefully blotted between tissue paper, put in a closed flask and weighed. From this the total mass uptake can be calculated. The absorbed liquid was distilled out of the membrane by a method described by Mulder et al [31] and subsequently collected in a cold trap cooled with liquid nitrogen. A relatively large amount of water was added to the small amount of, the still frozen, distilled liquid to prevent losses by evaporation and to obtain a homogeneous solution. The composition of this mixture can now be determined by GC-analysis. If the added amount of water to dilute the distillate is known, the total amount of organic component in the analysed diluted solution can be calculated. This amount should be equal to the absorbed amount of this component in the membrane. Because also the total mass uptake in the polymer film was determined, the composition of the absorbed liquid in the film can be calculated according to the equations given below.

$$\phi_i = \frac{m_i/\rho_i}{\sum_{j=1}^{n} (m_j/\rho_j)} \qquad \text{n=2 (3) for binary (ternary) systems} \qquad (15)$$

$$Y_i = \frac{m_i}{\sum_{j=1}^{2} m_j} \qquad (16)$$

$$\alpha^S_{i/j} = \frac{Y_i / (1-Y_i)}{X_i / (1-X_i)} \qquad (1-X_1 = X_2 \approx 1) \tag{17}$$

Sorption in pure liquids

For the determination of the crosslinking degree and the binary Flory-Huggins interaction parameters, sorption experiments were also performed in the pure organic liquids using a similar procedure as described above. From the mass increase of the polymer sample the composition of the swollen polymer sample can be determined according to equation (15).

5.4 RESULTS AND DISCUSSION

In this section the results of equilibrium sorption experiments will be presented. First the dominant role of the sorption step on the selectivity in the pervaporation of trace organics from aqueous solutions will be shown.

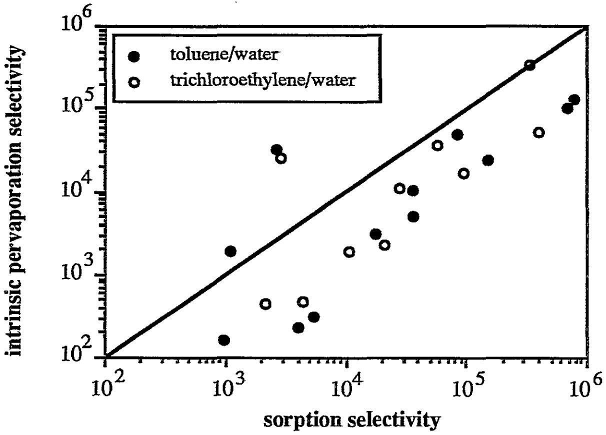

Figure 1: Correlation between intrinsic pervaporation selectivity and sorption selectivity

From previous work [16] permeability data are obtained. The intrinsic selectivities given in this paper were defined as:

$$\alpha^{i}_{oc/w} = \frac{\mathcal{P}_{oc}}{\mathcal{P}_{w}} \tag{18}$$

in which $\mathcal{P}_w$ represents the product of observed water flux [m^3/m^2-s] and membrane thickness [m]. The correlation between this selectivity factor and the selectivity factor for sorption defined by equation (17) is presented in figure 1.

The data are plotted on a double logarithmic scale, because the selectivities differ over more than three orders of magnitude for the elastomeric materials chosen. Obviously a strong dependence of pervaporation selectivity on the sorption behaviour of the polymer exists. The observed pervaporation selectivities are roughly a factor of 10 smaller than the sorption selectivities, indicating that diffusion rates are in favour of water. For two elastomers, epichlorohydrin terpolymer (ETER A) and neoprene (CR), the pervaporation selectivity is higher than the sorption selectivity, which is surprising, but has not been further investigated.

5.4.1 The solubility parameter approach

The three dimensional solubility parameters of the elastomers are given in table 1 both calculated from group contributions [24] and taken from literature [21, 23, 32]. In the case of polyurethane, poly acrylate rubber and the fluorocarbon elastomer the exact chemical structure of the polymer is unknown. For polyurethane the parameters for polytetramethylene glycol adipate are given. The solubility parameters for the acrylate rubber are based on values for polyethylacrylate. A 70/30 copolymer of polyvinylidenefluoride and polyhexafluoropropylene is used in the calculation of the solubility parameters for the fluorinated rubber. The calculated values are compared to data found in literature. In general there is a good agreement between experimental and calculated values. The calculated value for the 'polar solubility parameter' of polychloroprene, however, is probably too high [21], whereas in literature deviating values have been reported for the "hydrogen bonding parameter" of fluorinated elastomers [21].

The important role of polar interactions and the hydrogen bonding ability ($\delta_{p/h}$) on the water permeability in pervaporation has been shown elsewhere [16]. In contrast to this the polarity/hydrophilicity of the membrane was shown to be of only limited importance with respect to the permeability of the organic component. In figure 2 the contribution of polar/hydrogen bonding groups in the polymer to the sorption of water and thus to the permeability in the elastomeric membranes is shown.

Table 1: Solubility parameters of various elastomers and penetrants

		ρ	δ_d		δ_p		δ_h		$\delta_{p,h}$	
no	ELASTOMER	[g/cm^3]	calc	lit.	calc	lit.	calc	lit.	calc	lit.
1	Polybutadiene	0.89	15.5	17.5	0	2.3	0	3.4	0	4.1
2	Nitrile-Butadiene Rubber (18 % AN)	0.93	15.7	18.3	4.3	5.6	2.8	3.7	5.1	6.7
3	Nitrile-Butadiene Rubber (28 % AN)	0.95	15.5	18.7	6.9	7.4	3.5	3.9	7.7	8.4
4	Nitrile-Butadiene Rubber (38 % AN)	0.97	16.0	19.1	9.7	9.2	4.2	4.1	10.6	10.1
5	Polychloroprene	1.21	16.0	19.4	7.7	3.1	2.4	2.7	8.1	4.1
6	Epichlorohydrin terpolymer	1.33	16.8	18.6	9.8	8.2	7.0	7.2	12.0	10.9
7	Acrylate rubber	1.15	16.5		5.7		9.0		10.7	
8	Polyoctenamer	0.87	16.0		0		0		0	
9	Ethene-propene terpolymer	0.85	16.0	18.0	0	0.8	0	2.1	0	2.2
10	Polydimethyl siloxane	0.97	-	16.0	-	0.1	-	4.7	-	4.7
11	Polyurethane	1.15	16.9	17.4	5.6	5.1	9.0	10.2	10.6	11.4
12	Fluorinated elastomer	1.69	14.0	15.3	7.8	7.2	0	5.3	7.8	8.9
	PERMEANT									
	toluene	0.87		18.0		1.4		2.0		
	trichloroethylene	1.46		18.0		3.1		5.3		
	water	1.00		19.5		17.8		17.6		

Figure 2 shows a satisfactory correlation for the sorption of water with the 'combined solubility parameter'. The sorption of water is enhanced, when the polar/hydrophilic character, indicated by $\delta_{p,h}$, increases. On a similar scale as above data for the sorption of the organic component from aqueous solutions are plotted in figure 3. The solubility of the organic component appears to be almost independent of the solubility parameter for polar interactions and hydrogen bonding ($\delta_{p/h}$).

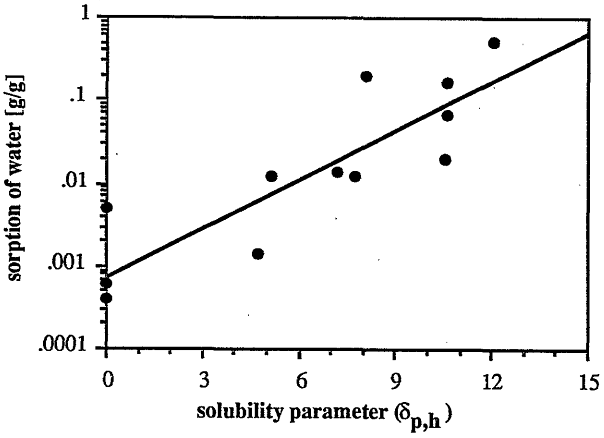

Figure 2: Water sorption for several elastomers as a function of the combined solubility parameter for polar and hydrogen bonding contributions; $\delta_{p,h}$

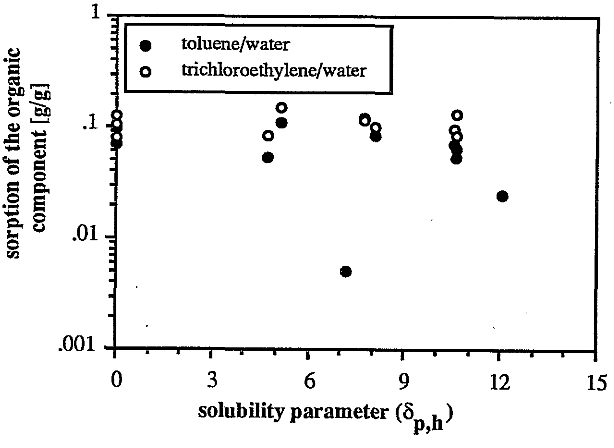

Figure 3: Sorption of the organic component for several elastomers in binary aqueous solutions as a function of the combined solubility parameter for polar and hydrogen bonding contributions; $\delta_{p,h}$

From the two figures shown above a tentative conclusion can be drawn. With respect to the sorption behaviour of elastomeric membranes in binary aqueous solutions of toluene or trichloroethylene a strong dependence of the water sorption on the chosen elastomeric membrane material is observed. The sorption of the organic component in the membranes gives an almost constant sorption value independent of $\delta_{p,h}$, which implies that other factors (diffusion) determine the differences in permeability observed for this component [16].

Determination of diffusion coefficients in the membrane falls beyond the scope of this work. If solubility data are used, however, in combination with permeability data obtained previously [16] an indication of this transport parameter may be obatined using $\mathcal{P}=\mathcal{D}.S$. A satisfactory correlation (not shown in this paper) with the glass transition temperature is obtained, which confirms the previously drawn conclusion that the transport rate of the organic component is governed by the diffusion rate of this component in the membrane.

The transport rate of water, on the other hand, will be minimal in hydrophobic membranes, due to the extremely low sorption values. Hence very small water fluxes and extremely high selectivities will be observed. It is concluded that high selectivities are not based on high organic component fluxes but rather on very low water fluxes.

5.4.2 Flory-Huggins thermodynamics

Equations (13) and (14) have been used to calculate the preferential sorption in elastomeric pervaporation membranes. The interaction parameters χ_{13} and χ_{23} are calculated from the sorption of the pure components in the elastomer (from equations (10) and (12), see below). The physical properties of the components from the liquid binary mixtures used for the calculation of the liquid/liquid binary interaction parameters are summarized in table 2 (column 2-4).

Determination of the liquid/liquid interaction parameter (χ_{12})

For the determination of binary liquid/liquid interaction parameters in aqueous solutions equation (10) can be used. This equation can be solved with the solubilities of toluene and trichloroethylene in water given in the fifth column of table 2 and an activity of 1 per definition at the solubility limit for systems with a poor mutual solubility. The binary liquid/liquid interaction parameters thus calculated are given in the last column of table 2.

Table 2: Physical properties of liquids used

component	density [g/cm^3]	molar volume [cm^3/mole]	molecular weight [g/mole]	solubility in water [cm^3/cm^3]	χ_{12}
water	1.00	18.0	18.0	-	-
toluene	0.87	107	92.2	0.00063	12.2
trichloroethylene	1.46	90.2	131.4	0.00075	11.2

Determination of the polymer/water interaction parameter (χ_{23})

The value of the polymer/water interaction parameter can easily be evaluated from equilibrium sorption experiments. A problem, however, is the continuous mass uptake in NBR-membranes. Even after more than 1000 hours of sorption, equilibrium is not reached as illustrated in figure 4.

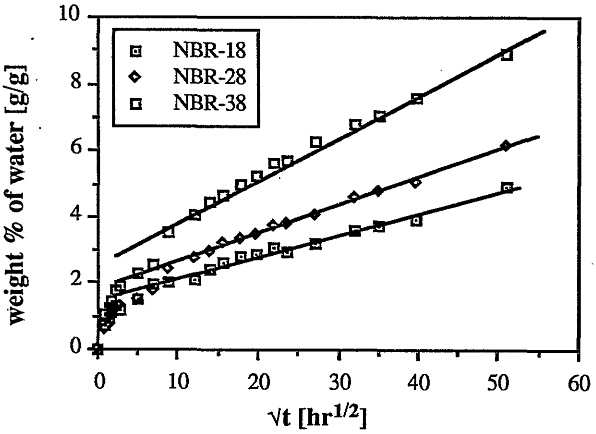

Figure 4: Water uptake as a function of the square root of time in NBR-membranes

Several authors already observed these phenomena in elastomers and attributed this to oxidative breakdown of primary bonds [8]. Brun et al. [33], however, pointed at the possibility of water clusters being formed. Plotting the relative mass uptake as a function of the square root of time, after an initial stage a direct proportionality is shown, which could indicate that an extremely slow diffusion process is going on. Arbitrarily the absorbed amount of water in NBR membranes was determined from a plot of the volume fraction of liquid in the swollen film as a function of the concentration of organics in the aqueous solution (fast swelling processes). The intercept with the Y-axis gives the absorbed amount of pure water (ϕ_2). With the data thus obtained, summarized in the second column of table 3, the polymer/nonsolvent interaction parameters as given in the third column of table 3 can be calculated using equation (10).

Table 3: Volume fractions of water in various elastomers and the calculated binary interaction parameters (χ_{23})

polymer	ϕ_2	χ_{23}
BR	0.0091	3.8
NBR (18)	0.013	3.4
NBR (28)	0.029	2.7
NBR (38)	0.048	2.3
PDMS	0.0014	5.6
EPDM	0.00067	6.3

Determination of the polymer/solvent interaction parameter (χ_{13})

Binary polymer/solvent interaction parameters were obtained from literature in cases where such data were available (see table 4). A swelling experiment in a solvent (lit.solvent; column 3) with a known value for the binary interaction parameter (χ(lit); column 2) is performed. The molecular weight between cross-links (M_c; column 5) can be calculated from the experimental polymer volume fractions obtained (ϕ (lit.solv., column 4) according to equation (12). Binary interaction parameters for other pure solvents can now be determined from swelling experiments (column 6-10) using this M_c-value. Essential in this case is that the measurements are performed using membranes which have been cross-linked at identical conditions. This procedure has been followed for PDMS with a literature given interaction parameter for toluene of 0.465 [34, 35]. At lower degrees of swelling the interaction parameter increases upto a value of 0.72 at a solvent volume fraction of 0.20 [35]. Literature interaction parameters were also obtained for benzene/BR

[13] and hexane/EPDM [14]. For the latter polymers no interaction parameters were found for toluene or trichloroethylene. For toluene/BR an interaction parameter has been calculated using data given in the pertinent paper. An interaction parameter for trichloroethylene/BR has been calculated following the procedure given above. For the terpolymer of ethylene and propylene a concentration independent interaction parameter has been found for n-hexane. This interaction parameter has been used to calculate an average molecular weight between crosslinks and the interaction parameters for toluene and trichloroethylene. The physical properties of the elastomeric materials involved are given in table 5.

Table 4: Literature values for interaction parameters, experimental polymer volume fractions, calculated molecular weights (M_c) and calculated interaction parameters (χ_{13})

elastomer	χ_{13}(lit)	lit. solv.	ϕ_3 (lit. solv.)	M_c [g/mole]	ϕ_3 (tol)	χ_{13}(tol)	ϕ_3(tri)	χ_{13}(tri)
BR [13]	0.33	toluene	0.262	1900	0.262	0.24	0.440	0.60
PDMS [34]	0.465	toluene	0.451	1000	0.451	0.465	0.396	0.40
EPDM [14]	0.25	hexane	0.411	800	0.398	0.30	0.291	0.04

Table 5: Physical properties of the elastomers involved

polymer	**density [g/cm^3]**	**Mol. weight (M_n) before crosslinking [g/mole]**
BR	0.90	182,200
NBR (18)	0.93	87,100
NBR (28)	0.95	72,700
NBR (38)	0.97	70,600
PDMS	0.98	n.d.
EPDM	0.86	n.d.

In the absence of interaction parameter data for the NBR-membranes, values have been obtained by a procedure proposed by Bhatnagar [12, 13]. Polymer films containing different amounts of the cross-linking agent dicumylperoxide (DCP) have been heat treated to produce a cross-linked polymer network. If the cross-link efficiency is independent of the concentration of DCP, the molecular weight between crosslinks will be inversely proportional to the added amount of DCP. Equation (12) can be solved by an iteration procedure. In table 6 first the polymer volume fractions for two crosslinked elastomers in pure toluene are given, whereas in the fourth and fifth column the results of an iteration procedure are given with respect to the molecular weight between crosslinks and the binary interaction parameter respectively. The pure solvent swelling data with respect to trichloroethylene are given next, from which a polymer/trichloroethylene interaction parameter can be calculated using the calculated molecular weight (M_c) of column 4.

Table 6: Pure liquid sorption data, calculated binary interaction parameters and molecular weights (M_c) for NBR membranes

elastomer	**ϕ_3(tol)**		**M_c (2% DCP) [g/mole]**	**χ_{13}(tol)**	**ϕ_3(tri)**	**χ_{13}(tri)**
	1% DCP	**2% DCP**			**2% DCP**	
NBR (18)	0.242	0.325	1900	0.40	0.258	0.28
NBR (28)	0.302	0.354	5100	0.59	0.295	0.57
NBR (38)	0.354	0.399	5200	0.63	0.301	0.58

Concentration dependent equilibrium sorption experiments

Equilibrium sorption experiments have been carried out for the highly apolar/hydrophobic EPDM and PDMS elastomeric membranes, as well as for a range of copolymers of butadiene and acrylonitrile with varying polarity and hydrophilicity. As an example of these experiments a sorption isotherm is presented in figure 5 in which the closed circles represent the experimentally determined sorption values of the organic component. It is evident from this figure that the partition coefficient can be assumed to be of the "Henry-type" only at low concentrations. This means that in this concentration range the solubility of the organic component in the membrane is directly proportional with its concentration in the binary liquid mixture. Calculated partition coefficients obtained by a linear regression fitting procedure in the low concentration range are tabulated in table 7.

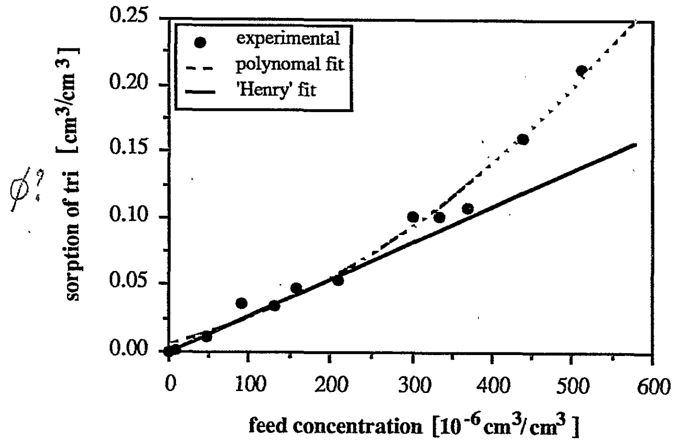

Figure 5: Volume fractions of liquid in a NBR(18) membrane as a function of the composition of aqueous mixtures of trichloroethylene

Table 7: Solubility coefficients ($S_{M/L}$) for the organic component

	solubility coefficient	
elastomer	**toluene**	**trichloroethylene**
BR	393	304
NBR (18)	385	289
NBR (28)	408	237
NBR (38)	359	209
PDMS	200	172
EPDM	394	176

Quite remarkable in table 7 is the sorption behaviour of the organic components in NBR-copolymers, for which only little dependence on the polarity or hydrophilicity of the polymer is found. The PDMS membranes surprisingly exhibit lower interactions with the organic components, especially for toluene, compared to the butadiene-acrylonitrile copolymers which is evidenced from the larger calculated partition coefficients for the NBR copolymers in table 7.

Comparison of calculated and experimental sorption isotherms

The experimental sorption data as presented above have been compared with theoretical values obtained from equations (13) and (14). A rough estimation of the activity coefficient was obtained before, from solubility data ($1/\phi_{sat}$ giving 1587 and 1333 for toluene and trichloroethylene respectively). The activity coefficient for the organic component will now be calculated more accurately from actual sorption experiments in aqueous solutions, using equation (13). A concentration independent activity coefficient for toluene and trichloroethylene in water is obtained from the ternary Flory-Huggins model. The activity coefficients from the experimental swelling data for NBR(38) membranes in liquid binary mixtures of toluene (250 μg/g) and trichloroethylene (500 μg/g) are 1026 and 854 respectively. These activity coefficient values have been used in all model calculations for different elastomers. The binary liquid/liquid interaction parameters (χ_{12}) can now be recalculated on the basis of the new values for the activity coefficient. The binary interaction parameter for toluene/water and trichloroethylene/water are re-estimated to 11.9 (previously 12.2) and 10.8 (previously 11.2) respectively. These small modifications did not affect the calculations to obtain the theoretical swelling values. As can be seen from the figures 6 and 7 the theoretical sorption values from the ternary Flory-Huggins equations are in good agreement with the experimental values for NBR(28) membranes.

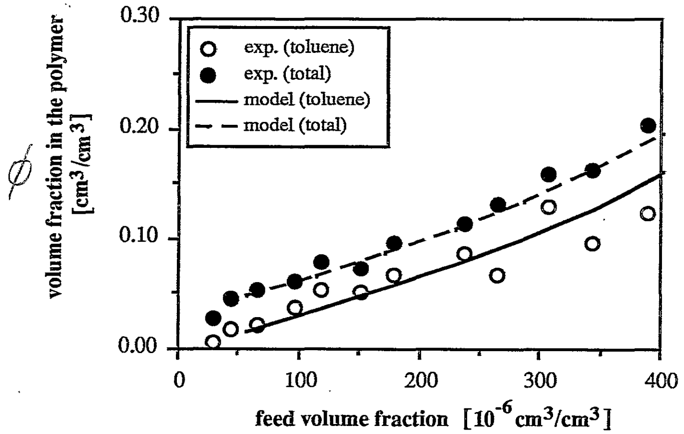

Figure 6: Volume fractions of liquid in a NBR(28) membrane as a function of the composition of aqueous solutions of toluene

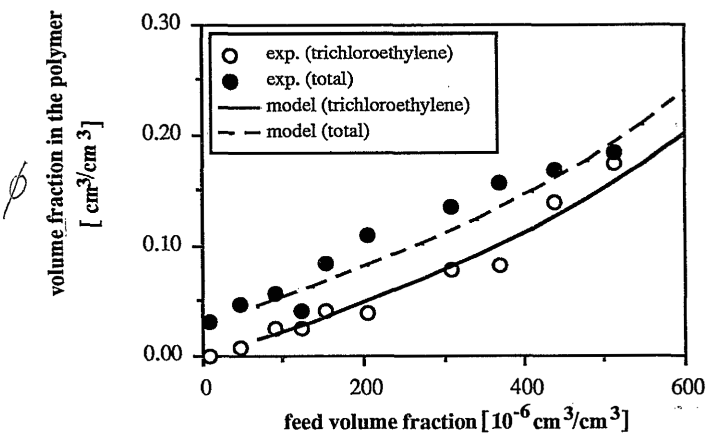

Figure 7: Volume fractions of liquid in a NBR(28) membrane as a function of the composition of aqueous solutions of trichloroethylene

In table 8 the calculated and experimental total sorption values are summarized for one specific concentration range of toluene/water (365 - 401 * 10^{-6} cm^3/ cm^3) and trichloroethylene/water (510 - 585 *10^{-6} cm^3/ cm^3) mixtures. In these concentration ranges extensive sorption experiments have been performed, in order to obtain very accurate sorption values. In general only small deviations between experimental and theoretical values are observed. Deviations must be due to concentration dependence of the binary interaction parameters.

For PDMS a concentration dependence of the binary interaction parameter for toluene has been reported [35]. If the higher value from literature for the toluene/PDMS interaction parameter is used in the theoretical equations, a considerable improvement of the model prediction of sorption values is established (see table 8). A comparison of theoretical and experimental values in the case of trichloroethylene sorption from aqueous solutions in EPDM was not carried out. The very low interaction parameter obtained from pure liquid swelling experiments (see table 4) gives unrealistic high sorption values. A possible explanation for this fact is given by Frensdorff [14]. He showed that the interaction parameter of an aromatic compound (benzene) is only affected to a minor extent by the adsorbed amount of liquid, whereas the interaction parameter for chlorinated hydrocarbons (methylchloride) depends strongly on the solvent concentration (< 30%) in the swollen sample.

Resuming it is concluded that as a first approximation the use of literature values for χ_{13} can provide a rough estimation of the sorption behaviour of elastomeric membranes. For more exact estimations the Flory-Huggins interaction parameters should be determined for the actual elastomers, whereas their concentration dependence has to be carefully evaluated in some cases.

Table 8: Calculated and experimental values for the total liquid sorption from aqueous solutions in several elastomers

	TOLUENE			**TRICHLOROETHYLENE**		
elastomer	**feed conc. [10^{-6} cm^3/cm^3]**	**total liquid vol. fract.**		**feed conc. [10^{-6} cm^3/cm^3]**	**total liquid vol. fract.**	
		exp.	**calc.**		**exp.**	**calc.**
BR	391	0.185	0.172	555	0.165	0.159
NBR (18)	382	0.173	0.182	510	0.213	0.219
NBR (28)	365	0.203	0.183	510	0.184	0.183
NBR (38)	401	0.203	0.218	555	0.229	0.232
PDMS [34]	365	0.078	0.112	585	0.107	0.172
PDMS [35]	365	0.078	0.083			
EPDM	399	0.127	0.138			

The molecular weight between crosslinks of the elastomeric network is very important in the case of sorption of pure liquids. The degree of cross-linking, however, is of only minor importance for the sorption of organic components from aqueous solutions (in the concentration range of interest), as becomes clear from figure 8. The two curves represent the calculated sorption behaviour in a non-crosslinked and a crosslinked elastomer with a molecular weight of the crosslinked unit of 1900 g/mole respectively. For comparison of experimental and theoretical values the observed total liquid up-take is given in figure 8 too. Again a satisfactory correlation of experiment and theory is observed.

In most practical applications the extent of swelling is quite low and equations (13) and (14) can be simplified by neglecting the crosslinking term in the right hand side of the equation. These simplified equations can now be used to determine the volume fractions of the permeants in the membrane as a function of the liquid feed concentration at the membrane interface. With the equations presented in a previous paper [36] the concentration at the membrane interface can be determined as a function of cross-flow velocity. Therefore experiments should be performed in pervaporation cells with well defined dimensions, which allows an accurate estimation of the Reynolds number and other dimensionless hydrodynamic quantities. The concentration at the membrane interface will often be a factor of 10 lower than in the bulk feed solution due to concentration polarization phenomena. A 'Henry-type' of partition coefficient can therefore properly be assumed. This assumption was already made implicitly in the mass transfer resistance-in-series model [15], which provides the basic equations for describing the transport of the organic component in the pervaporation process.

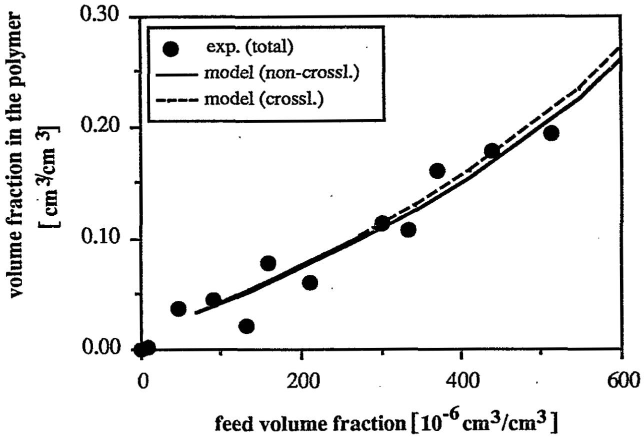

Figure 8: Effect of crosslinking on the total sorption in NBR(18) membranes from aqueous mixtures of trichloroethylene

5.5 CONCLUSIONS

The investigated membranes show a wide range of sorption selectivities (three decades). In all cases the preferentially permeating organic component is also sorbed preferentially. The determining step in the selective transport is the preferential uptake of the organic component.

Solubility parameters for elastomeric pervaporation membranes can be calculated by means of additive group contributions provided that the molecular structure is known. A rough indication of the solubility of aqueous solutions in elastomers can be obtained on the basis of calculated $\delta_{p/h}$ -values. Sorption of water is almost completely excluded in elastomers with a low ability for polar interactions and hydrogen bonding (low value for $\delta_{p/h}$). Sorption of the organic component is relatively independent of this combined solubility parameter.

The sorption behaviour of elastomeric membranes with aqueous solutions of volatile organics is properly assumed to be of the 'Henry-type' in the low concentration range. With Flory-Huggins thermodynamics a good description is given of this sorption behaviour. Volume fractions in the swollen polymer film in binary aqueous solutions have been calculated using experimental interaction parameters and ternary Flory-Huggins equations. The agreement between experiment and theory is quite satisfactory, when binary interaction parameters are determined from sorption experiments of pure liquids in actual systems. For different NBR copolymers, the interaction parameters and the molecular weight between cross-links (M_c) have been determined for different degrees of cross-linking. The cross-link term is very important at the high swelling values obtained with pure liquids. However, for sorption experiments with relatively low concentrations of the organic component in water this elastic term is of minor importance and can be neglected.

5.6 LIST OF SYMBOLS

a = activity [-]
$\mathcal{D}$ = diffusion coefficient [m^2/s]
J_i = pervaporation flux of component i [m^3/(m^2.s)]
M = molecular weight [g/mol]
$\mathscr{m}$ = absorbed amount [g]
$\mathcal{P}$ = permeability [m^2/s]
S = solubility coefficient [-]
V = molar volume [cm^3/mole]
x = distance in the membrane [m]
X = composition of the binary liquid mixture [g/g]
Y = composition of the absorbed liquid [g/g]

Greek symbols

α = selectivity [-]
χ = Flory-Huggins interaction parameter [-]
δ = solubility parameter $[J^{1/2}/cm^{3/2}]$
ϕ = volume fraction $[cm^3/cm^3]$
γ = activity coefficient [-]
ρ = density $[g/cm^3]$

Subscripts

c = crosslinked unit
d = dispersion
h = hydrogen bonding
i = component i
j = component j
1 = preferential permeating component (solute)
2 = less permeable component (solvent)
3 = polymer
L = liquid
M = membrane
oc = organic component
p = polar
w = water

Superscripts

m = membrane
PV = pervaporation
S = sorption
sat = saturated
w = membrane/feed side interface (in the feed)
∞ = infinite dilution

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CHAPTER 6

TECHNICAL AND ECONOMIC EVALUATION[¥]

H.H. Nijhuis*, M.H.V. Mulder*, M.C.H. van Drunen# and C.A. Smolders*

SUMMARY

At present, volatile organic components are removed from ground water, surface water or aqueous waste streams through activated carbon adsorption or air stripping. Pervaporation, a relatively new membrane filtration process, removes the volatile organics very selectively. On the basis of a scale-up study, described in this paper using parameters from laboratory experiments, this process has shown good prospects in this field.

From an accounting viewpoint the different processes have been compared on the basis of two potential applications. In the first case a small-scale process is considered, typical for ground water sanitation. The second case is dealing with a large-scale waste water purification system, typical for industrial waste water treatment. The evaluation has been carried out for single processes as well as for hybrid systems.

Besides the attractiveness from a technical point of view, the pervaporation process shows also good prospects from an economic point of view . The costs for this process vary from Dfl 0.83 to Dfl 1.86 per m^3 of water treated, depending on product recovery and module type chosen. Depending on the feed flow rate, the concentration and kind of the contaminants the costs for alternative processes are Dfl 0.34 to f 5.30 per m^3 of water treated.

6.1 INTRODUCTION

In an alternative choice problem some alternative courses of action are specified and many times a choice is made on a strictly judgmental basis. More fundamental based decisions are restricted often to economic considerations (finding the cheapest alternative), because this is in most cases the only variable that can be evaluated on a quantitative basis. Cost calculations, however, are very rough, whereas future developments are hard to foresee.

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* Department of Chemical Technology
# Department of Business Administration

Often other nonquantitative considerations play a very important role in reaching a decision on the alternative to be chosen. Therefore the analysis of alternative choice problems should involve the following steps [1]:

1. Define the problem.
2. Select possible alternative solutions.
3. Measure and weigh those consequences of each selected alternative that can be expressed in quantitative terms.
4. Identify those consequences that cannot be expressed in quantitative terms and weigh them against each other and against the measured consequences.
5. Make a decision.

Problem definition and alternative solutions

In the Netherlands and many other countries all around the world ground water supplies are severely polluted with volatile organic compounds (VOC's), which can be divided into two main categories:

- aromatic hydrocarbons: benzene, toluene, styrene and xylene
- chlorinated hydrocarbons: chloroform, tetrachloromethane, trichloroethylene, perchloroethylene.

VOC contamination of ground water is typically caused by leakage of underground storage tanks, poor disposal practices or accidental spills. This variety of causes, coupled to the small quantity of VOC's required to already cause significant contamination, makes preventive action very difficult. Removal of such organic traces, of which several appear on either the so-called 'black list' or the 'high-priority list', from waste water is essential because they are a continuous threat to the public health. Today two processes are available, being *activated carbon adsorption* and *air stripping*, whereas *pervaporation* is a rapidly developing process, which is available on a pilot plant scale.

Approach

The introduction of new techniques always should involve a solid analysis of costs and profitability. The profits of installing a ground water or waste water purification system are difficult to determine, because they can only be expressed in what is called 'opportunity costs'. Anthony [1] gives the following definition of this concept:

> *"Opportunity cost measures the value of the opportunity which is lost when the choice of one course of action requires that an alternative course of action be given up".*

In this case the main opportunity costs are the costs for public health care. This aspect will be of major importance for a 'go/no-go decision'. It may be suspected that the public health costs will be extraordinary high. Therefore a go-decision for purification should always be made. The next step will then be to decide which particular purification system will be installed. Besides economic considerations several more technical aspects will play an important role in deciding for the most suitable process.

> *The aim of the present work is to evaluate, both from an economic and from a technical point of view, the feasibility of different processes, in removing volatile organic components from aqueous solutions.*

Therefore the technical background of the different processes will be summarized briefly in order to get an impression of the most important process parameters. Because limited practical experience on a technical scale is available concerning the removal of trace organics from water by pervaporation, experiments have been performed on a semitechnical scale to determine the problems occurring during scale-up. The pervaporation unit used and the results obtained are also described in this paper.

6.2 GENERAL TECHNICAL BACKGROUND

In the previous section the problem has already been defined. VOC's in ground water or waste water create an environmental problem which has to be solved by applying a process capable of removing these toxic substances. Two basic techniques are nowadays available, viz.:

- adsorption onto activated carbon
- air stripping.

From an environmental point of view the process of air stripping has to be combined with an additional process to treat the stripper off-gases. In principle three possibilities are available:

- gas phase activated carbon adsorption
- biofiltration
- membrane filtration (vapour permeation).

Finally the rapidly developing process of pervaporation can be mentioned for the direct removal of volatile organics from water. The state of the art of this relatively new membrane filtration process is at the threshold of commercialization.

In this section a general technical description will be given of the different processes. The aim is to get an understanding of the most important process parameters which should be considered and carefully evaluated in order to decide on the most effective alternative solution.

Liquid phase activated carbon adsorption

Activated carbon adsorption processes have already proven to be successful in several cases [2-5]. The technique is based on the adsorption of the component to be removed at the internal surface of the carbon particles. After the complete surface is occupied, the carbon has to be regenerated.

The costs of this process depend on the kind of pollutant, adsorption system and regeneration technique.

It is also possible to use a less expensive non-regenerable kind of activated carbon. Especially in cases where regeneration is a problem, because of the large variety of adsorbed substances, the use of less expensive carbon types seems to be a profitable option. The loaded carbon (containing upto 10% of VOC) may be burnt or brought, often against high costs, to a landfill. From an environmental point of view the latter option is not a very adequate solution.

Air stripping

Air stripping can also be applied to remove volatile organic components from aqueous solutions. Air or steam is brought in contact with the contaminated water to remove the volatile pollutant.

It is a relatively cheap technique of which the efficiency is determined by the air current, the length of the stripper column and the volatility of the organic component. To prevent that a water pollution problem is transferred to an air pollution problem the off-gases have to be treated afterwards.

Several options are available to treat the stripped gases of which gas-phase adsorption onto activated carbon [6-8] and biofiltration have proven to be the most promising [9-13]. Vapour permeation, a relatively new membrane process, could also be an attractive alternative, but has not been applied in combination with air stripping on a technical scale yet. Therefore this alternative solution will be considered only briefly in the evaluation.

Pervaporation

The first commercial pervaporation plants have been installed by a combination of a Dutch company SETEC with a German company GFT. Until recently the attention of SETEC/GFT (today part of Carbon-Lorraine) was primarily focussed on the dehydration of organic liquids, but now they are interested also in removing volatile organic contaminants from aqueous solutions. Other companies are interested and active in that area too [14, 15].

A liquid mixture is brought in contact with a membrane at the upstream side, whereas the permeate is removed as a vapour at the downstream side. This is established by reducing the relative vapor pressure at the permeate side through either the use of an inert carrier gas or an applied vacuum. The permeate is successively obtained in liquid form in a condenser. In the pervaporation of trace organics from water the pollutants are obtained as an almost pure liquid, whereas no additional substances (like activated carbon or micro-organisms) are required.

In this particular application of pervaporation three process parameters may be distinguished which determine to a large extent the process performance [16-24]:

- *module type*
- *the liquid cross-flow conditions at the membrane/liquid interface*
- *downstream pressure.*

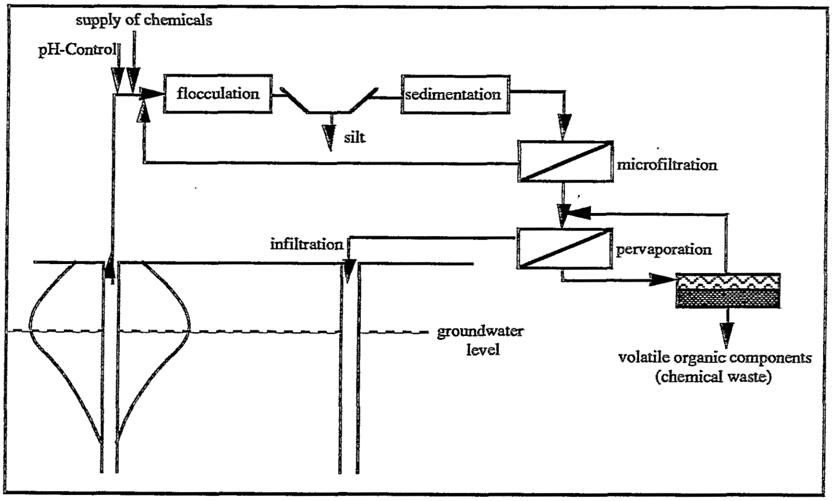

Figure 1: Schematic of ground water withdrawal in combination with pervaporation and infiltration of the purified water

Figure 1 gives an example of an in-situ process for the removal of volatile organic components from water. Pervaporation is combined with a ground water withdrawal system. Depending on the composition of the water, traditional ground water treatment techniques like flocculation, sedimentation and filtration can be very useful to remove relatively large sized particles. Suspended and colloidal materials can also be removed by a microfiltration process. In most cases, however, simple sand filtration will be a sufficient pretreatment before the aqueous mixture enters the pervaporation module. By infiltration of the purified water (retentate) the sanitation efficiency is increased, because the ground water level remains constant and the sewage costs are reduced. Similar set-ups will be used in the treatment of aqueous waste streams by other processes like air stripping or liquid phase activated carbon adsorption.

In the next two sections the process of pervaporation will be evaluated on a semitechnical scale. Extensive laboratory based pervaporation experiments have been performed in order to select a suitable membrane material and measure the effects of several parameters on the pervaporation performance [16-19]. Only scarce experience is available in large scale applications for this process, however, in contrast to activated carbon adsorption or air stripping based purification systems.

6.3 EXPERIMENTAL

The membrane material used in this study is polydimethylsiloxane (silicone rubber; PDMS). The membranes were prepared on a polymethylmethacrylate (PERSPEX®) plate in a casting machine. After cross-linking overnight at 70 °C the average membrane thickness was 110 μm.

The membranes were stacked successively in a plate-and-frame module with a total membrane area of 1.7 m^2, which was then installed in a standard SETEC installation, normally used in the separation of ethanol/water mixtures. For the removal of volatile organic components from water the system was modified as schematically represented in figure 2.

A large storage tank containing 250 liters of liquid feed mixture is connected to a packed column, in which two layers can be distinguished. In the present study the lower phase is the organic phase (trichloroethylene has a higher density than water), whereas the aqueous phase is found in the upper part of the column. Depending on flow rate and height of the organic phase column any desired concentration can be obtained after steady state operating conditions have been reached. Before the feed enters the membrane stack the concentration (influent concentration) is determined. Furthermore the feed flow rate and the outlet concentration (effluent concentration) of the membrane stack are measured.

Downstream a low pressure is provided by a vacuum pump. After the permeants have left this vacuum pump condensation takes place at atmospheric pressures. This circumvents the problems associated with low pressure condensation. The condensation part of the system consists of two condensers. In the first condenser most of the permeate is collected using tap water with a temperature of approximately 10 °C. Because of demixing two layers will be present, a trichloroethylene-rich phase and a water-rich phase, which can easily be separated from each other. A part of the permeated trichloroethylene will not be obtained in the first condenser and a second condenser operating at a much lower temperature is connected in series.

Because the system could not be operated at explosion-proof conditions, security measures were taken. The storage tank is flushed with a nitrogen flow and the oxygen concentration is registered continuously.

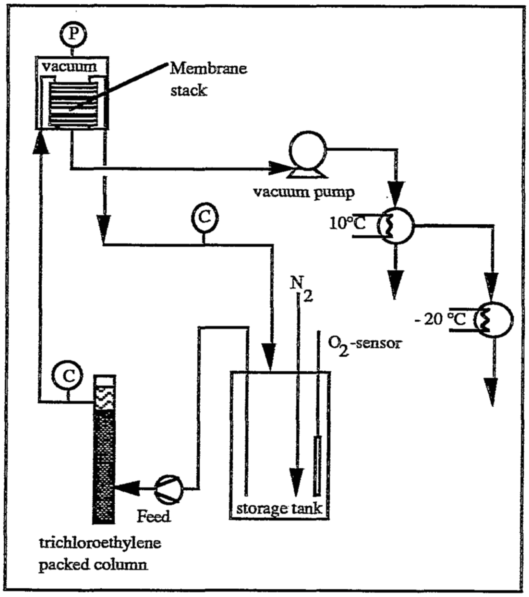

Figure 2: Schematic diagram of the experimental set-up

The membrane properties are characterized by two important parameters, the flux and the selectivity. The flux is defined as the amount of liquid permeating through the membrane per unit of time and per unit of active surface area [kg/m^2-h]. The selectivity of the membrane for a feed mixture is defined according to the equation below:

$$\alpha_{A/B} = \frac{(y_A/y_B)_{\text{permeate}}}{(x_A/x_B)_{\text{feed}}}$$

in which y_A and y_B represent the concentrations of components A and B in the permeate, whereas x_A and x_B represent the concentrations in the feed mixture.

6.4 RESULTS WITH A SEMITECHNICAL INSTALLATION

The installation has been in operation for two months separating 'synthetic' trichloroethylene/water mixtures of varying compositions. The system was operated at a feed flow rate of 22.8 l/hr, which appeared to be the maximal value. As a result of pressure build-up at the feed side the system started to leak at higher feed flow rates.

The results obtained with the installation are presented in the figures below. In figure 3 the flux of trichloroethylene and in figure 4 the composition of the permeate are given as a function of the liquid feed (influent) concentration at a temperature of 25 °C.

In comparison with our laboratory results obtained for similar silicone rubber membranes [16], both the flux and the selectivity are reduced in this semitechnical set-up. The total permeate fluxes are in the range of 7.5-31 g/m^2-hr, whereas an overall module selectivity factor of 500 can be calculated on the basis of data presented in figures 3 and 4. In this calculation a concentration drop over the membrane stack is taken into account. An intrinsic value of 20,000 for the selectivity factor obtained from laboratory experiments indicates that scale-up problems are definitely present. Compared to laboratory experiments the semitechnical pervaporation set-up operates at higher pressures at the permeate side, which can have a drastic effect on the pervaporation performance [20]. Another important deviation from our laboratory test conditions are the cross-flow velocities at the membrane/liquid interface.

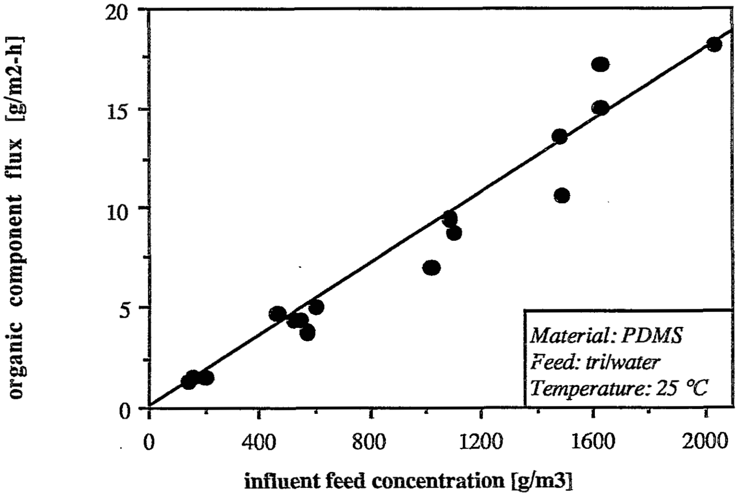

Figure 3: Flux of trichloroethylene as a function of the liquid feed concentration

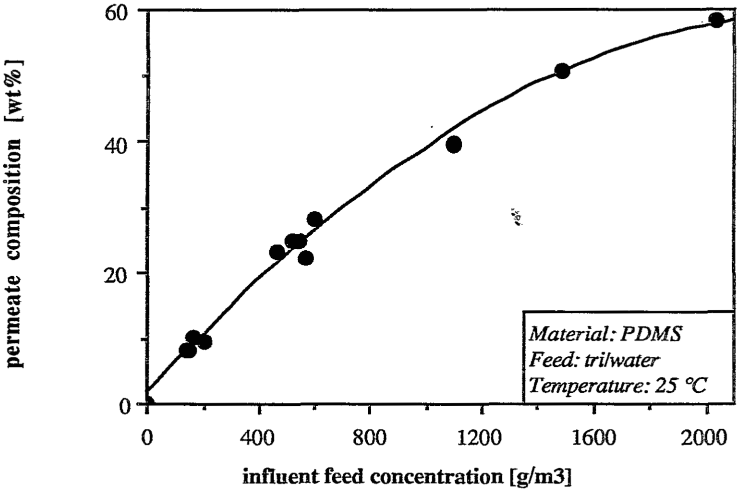

Figure 4: Composition of the permeate as a function of the liquid feed concentration

The influence of flow conditions on the performance of the pervaporation process is already extensively discussed elsewhere [17, 21, 22]. A rough estimation shows that the value of the overall mass transfer coefficient is $3 * 10^{-6}$ m/s under the conditions applied in this study. This is a low but not an unrealistic value for simple plate and frame modules. In the treatment of aqueous solutions of VOC's also other module types have been applied. For a spiral-wound system (0.3 m^2) and a small hollow fiber module (0.0035 m^2), the average overall mass transfer coefficient can be estimated to 2.10^{-5} m/s and 5.10^{-5} m/s respectively [22, 23].

This suggests already that other module types might operate more effectively in the removal of VOC's from water.

The observations given above, the effect of membrane thickness as well the extremely important effects of hydrodynamic conditions and permeate pressure, are taken into account in the next section, where the total operating costs for all alternative processes will be determined.

6.5 ECONOMIC EVALUATION

The different processes including pervaporation, will now be evaluated from an economic point of view on the basis of two possible separation problems:

- case I: ground water sanitation
- case II: off shore waste water treatment.

Both cases are fictive, but based on actual facts. For case I, typical for ground water sanitations, a relatively moderate concentration and a relatively low feed flow rate are considered, whereas for case II, typical for industrial waste waters, high concentrations and high feed flow rates have been evaluated. First the outlines of the two cases are presented, followed by the assumptions in the evaluation. The total operating costs have been determined on an annual basis and per m^3 of water handled for the different processes and the two cases. If possible, relations have been made between the costs and the most important process parameters to predict effects of changing process conditions on the total operating costs. As a result of the evaluation in the forthcoming sections the cheapest process can be selected.

Outline of case I

The first location described here was selected on the basis of detailed information available on the relation of sanitation costs and efficiency of several sanitation alternatives (in which pervaporation had not been included) [25-26]. The soil at the contaminated site, where liquids for the degreasing of metal parts were regenerated, appeared to be severely contaminated with chlorinated hydrocarbons of which tetrachloroethylene was found in the highest concentrations (20 g/m^3). At five points in the most contaminated area 10 m^3/h of groundwater should be withdrawn and purified through a liquid phase activated carbon process. In table 1 the fixed process parameters for this case are summarized.

Outline of case II

This case describes the waste water treatment on oil platforms. In contrast to case I relatively little is known about this location of contamination. Until now the waste water, which is almost completely saturated with low and high molecular weight hydrocarbons, is drained into the sea. It is expected that very soon international regulations will be proclaimed to restrict the drainage of these highly polluted waste waters. The off-shore treatment of waste water from drilling platforms, however, requires special conditions. Thermal incineration of the pollutants on-site is excluded, because of the explosion danger. Furthermore the purification unit has to be as small as possible, both in weight and volume, because of space restrictions on the platforms. Table 1 lists the specific process parameters and their values used in the analysis.

Table 1: System design parameters and values

CASE	**I** [25,26]	**II** [27]
Average influent concentration:	10 g/m^3	500 g/m^3
Flow rate:	10 m^3/h	500 m^3/h
Recovery	99 %	99 %
Sanitation hours per year	8,000	8,000

General assumptions for the cost evaluation

The investment and total operating costs of the processes have been evaluated. In determining the total investment costs, the costs with regards to production of ground water withdrawal points, connections from the pump station to the units and from the units to the sewer or to the infiltration point will not be taken into account. For ground water sanitations these latter installation costs will increase the total investment costs with approximately Dfl 10,000.- [28].

The total investment costs have been estimated with the help of data from experiments described in literature for similar scale problems. If such data were absent a commonly used relation as given by Peters and Timmerhaus has been applied [29].

$$\frac{\text{costs of equipment A}}{\text{costs of equipment B}} = \left(\frac{\text{capacity equipment A}}{\text{capacity equipment B}}\right)^n$$

A value for n of 0.6 should be used for activated carbon adsorption processes [30], whereas the same value has been used to estimate the investment costs for biofiltration [9, 10].

The total operating costs have been subdivided in three main categories:

- depreciation and interest
- labour and maintenance
- energy

Furthermore for activated carbon processes costs for replacement or regeneration of the activated carbon have been taken into account, whereas in pervaporation membrane replacement has been considered.

Table 2: Standard costs in the cost evaluation.

Depreciation	15 % of the investment costs
Labour	Dfl 40.-/hr
Electricity	Dfl 0.20/kWh
Refrigeration (cryo-unit)	Dfl 0.05/kg condensed
Regenerable carbon	Dfl 8.-/kg carbon
Nonregenerable carbon	Dfl 6.-/kg carbon
Regeneration on-site	Dfl 0.50-/kg carbon

The annual liquid feed pump energy costs are estimated at Dfl 2,000.- for a feed flow rate of 10 m^3/h, whereas they are assumed to increase linearly with increasing feed flow rate. In the air stripping process the liquid feed energy costs were assumed to be higher than in the liquid phase carbon adsorption process due to the height of the stripper column to which the water has to be pumped. An increase by a factor of 2 has been assumed. In the case of a hybrid process additional energy is required for conduction of either the liquid or the gas to the second unit.

Labour and maintenance costs for the small scale process were assumed to reflect to 1 person for 2 hours per day, whereas it has been assumed that for hybrid processes additionally 1 hour of labour and maintenance will be required. Due to the complexity of the biofiltration process probably 2 hours per day will be required to operate this process. For the large scale process, labour and maintenance costs are based on 2 persons at 8 hours per day. Furthermore it is assumed that additionally 1 person at 8 hours per day is required in hybrid operations, whereas in biofiltration systems probably 2 persons at 8 hours per day will be required. The standard costs in the calculations are summarized in table 2.

6.5.1 Investment and total operating costs for activated carbon adsorption

In this section the costs are presented to operate a liquid phase activated carbon adsorption process. The effects of the carbon loading capacity and the costs for regeneration will be included in the cost evaluation. Technical details on regeneration, loading capacity and system design are given in appendix A.

The data for calculating the costs of the small-scale activated carbon adsorption process have been obtained from the company, which installed the purification units for cleaning the ground water for case I [28]. The investment costs of a unit containing 1,600 kg of activated carbon were estimated at Dfl 60,000. -, which seems in reasonable good agreement with the investment costs for a somewhat larger installation [31]. For the large scale process 10 adsorbers are required, each containing 9,000 kg carbon, which would bring the investment costs to an average value of Dfl 1,700,000.- [2, 32].

Tabel 3: Costs of liquid phase activated carbon adsorption (see also appendix A)

CASE	I	II
Investment costs	60,000	1,700,000.-
Depreciation and interest	9,000.-	255,000.-
Labor and maintenance	26,400.-	211,200.-
Liquid pump energy	2,000.-	100,000.-
Carbon replacement	120,000.- (10 times/year)	720,000.- (1 time/year)
Regeneration on-site (Dfl 0.50/kg)		20,000,000 (444*10*9000 kg/year)
TOTAL ANNUAL COSTS	Dfl 157,400.-	Dfl 21,286,200.-
Costs per m^3 of treated water	**Dfl 1.97**	**Dfl 5.32**

In table 3 the investment costs and total operating costs for the two cases are summarized. It is obvious that in this concentration range and for the assumed loading capacity of 5% the largest contribution comes from the replacement or regeneration of the carbon.

On the basis of literature data [2, 28] the costs for removal, transportation, discharge of the loaded carbon, refilling and starting up can be estimated at about Dfl 12,000.- for the small scale process. Although the largest contribution comes from the costs of the activated carbon (Dfl 6.-/kg), labour costs also contribute to a large extent in the carbon replacement costs. The loading capacity of the activated carbon is in this sense an important process parameter; the higher the loading capacity the lower the annual replacement costs.

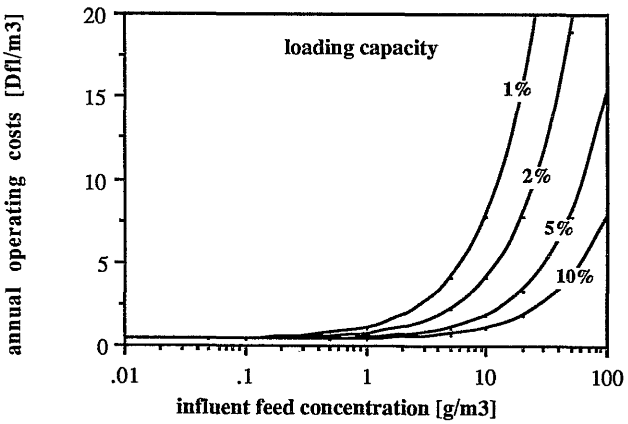

Figure 5: Total annual costs of liquid phase (10 m^3/h) activated carbon adsorption as a function of loading capacity and influent concentration

Effect of loading capacity

The importance of the loading capacity of the activated carbon is illustrated in figure 5 for a system treating 10 m^3/h. In this figure the costs per m^3 of treated ground water are presented as a function of the influent concentration and the loading capacity of the activated carbon. A value of Dfl 12,000.- for carbon replacement has been used in the calculations.

It is evident from this figure that the costs of the process are strongly related to the loading capacity of the carbon, especially at high influent concentrations. For low influent concentrations the total operating costs are independent of the carbon loading capacity and reflect the costs due to depreciation, labour and energy. In this range the total operating costs can be estimated at Dfl 0.34/m^3 water. In cases where the carbon has to be replaced frequently, regeneration of the activated carbon is often a profitable option. The effects of regeneration costs on the total operating costs are discussed below.

Effect of regeneration costs

Regeneration can be accomplished either on-site or carried out off-site by specialized companies. In literature a large variety of regeneration prices can be found ranging from about Dfl 0.01/kg carbon for steam regeneration on-site in gas phase activated carbon adsorption, when only steam and condensation costs are taken into account [32-34], to Dfl 2,-/kg carbon for regeneration off-site [35-36]. In figure 6 the total operating costs are presented as a function of the influent feed concentration and the price for regeneration for a system treating 500 m^3/h. As the upper limit of the carbon operating costs the price of non-regenerable carbon has been taken.

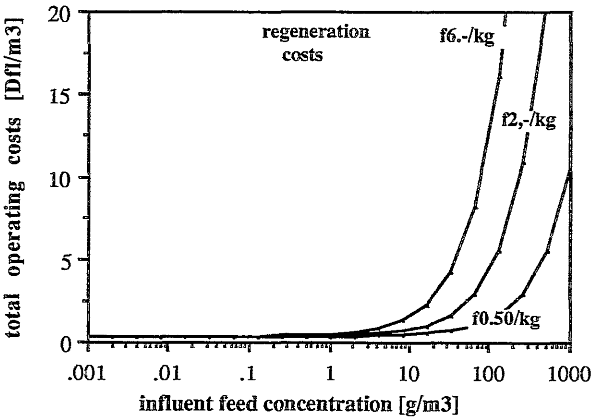

Figure 6: Total annual operating costs of liquid phase (500 m^3/h) activated carbon adsorption as a function of feed concentration and unit costs for regeneration (loading capacity 5%)

Figure 6 clearly indicates the drastic effect of the regeneration costs on the total operating costs.

In table 3 the regeneration costs have been fixed at Dfl 0.50/kg carbon, which seems to be an adequate value [6].

Résumé and comparison with literature data

It is important to emphasize that in literature on-site regeneration is not described for liquid phase carbon adsorption processes.

Therefore the technical feasibility of a liquid phase carbon adsorption process for large scale operations may be questioned (see appendix A).

Calculations have been performed and overall operating costs of Dfl 1.89 and Dfl 5.30/m^3 have been obtained for the small scale and the large scale process respectively.

Typical values for the costs of a liquid phase carbon adsorption process are given by Nyer [5]. The operating costs for treating ground water contaminants at levels of milligrams per m^3 range from \$ 0.21 - \$ 0.55/1000 gal (Dfl 0.12 - 0.29/m^3). The operating costs at contaminant levels of several grams per m^3 on the other hand increase substantially and range from \$ 0.48 - \$ 2.52/1000 gal (Dfl 0.25 - 1.32/m^3). Estimations are also given by others. Schröder [35-36] compared pervaporation and activated carbon adsorption at influent concentrations of 50 g/m^3 and estimated that activated carbon adsorption would cost Dfl 7.83/m^3. Such relatively high operating costs are also given by Grontmij [37] (Dfl 5.-/m^3).

Stenzel and Merz [2] reported on an actual case, in which ground water containing aromatic substances was treated with a total influent concentration of 8.7 g/m^3. The feed flow rate, however, was 4-5 times higher than that for the small-scale adsorption unit. The price per m^3 of contaminated ground water treated was fixed at Dfl 1.30, which is in reasonable agreement with our own results.

The results obtained above concerning liquid phase activated carbon adsorption indicate that the total operating costs can vary over a wide range depending on the concentration range involved, the loading capacity of the carbon and the possibility and the costs of regeneration (either on-site or off-site). In literature only systems are described in which the total carbon mass is removed after bed break through is observed. Regeneration on-site has been reported in several cases for gas phase activated carbon adsorption. This process may be applied in combination with air stripping as is shown in the next section.

6.5.2 Investment and total operating costs for air stripping based processes

In this section the total investment and operating costs for air stripping processes are presented. For the posttreatment of the exhaust gases biofiltration and gas phase activated carbon adsorption are considered. The application of gas phase carbon adsorption after air stripping seems an unnecessarily elaborate way to remove trace organics from water, because direct adsorption from the liquid phase is also possible. However, due to the improved selectivities (only the volatile organics will adsorb) and the improved performance (diffusion rates in the gas phase are higher than in the liquid phase) this alternative solution turned out to be an effective and profitable option. It seems possible to increase the loading capacity upto values of 10% for relatively 'dry' vapours [6, 32]. For more technical details on the processes considered one is referred to appendix B.

The investment and total operating costs are determined mainly by the recovery rate and the quantity of water that will be treated per unit of time and are rather independent of other parameters [6]. The example given below is therefore representative for the costs involved in the air stripping process.

In table 4 the costs for a treatment by means of a combination of air stripping and activated carbon adsorption or biofiltration are presented. Technical (small-scale) data were mainly obtained from an actual case [13], in which an air stripping process was applied to treat ground water contaminated with trichloroethylene and tetrachloroethylene. For large-scale air stripping processes technical and cost data were obtained from different sources. Fang and Khor [6] have written a comprehensive paper on the reduction of volatile organic compounds in aqueous solutions through air stripping and gas-phase carbon adsorption. In their paper the dimensions and installed column costs are given for various contaminating compounds. Furthermore the authors reported on the installed costs and power requirements of air stripping support facilities as well as on the specified total costs of air stripping. The energy costs are relatively high, because of the high air flow rates required. The power of the air blowers is assumed to be 7.5 kW and 3 * 30 kW respectively for the two cases surveyed in table 4. For the effects of carbon loading capacity and regeneration or replacement one is referred to the previous section. Although figures 5 and 6 were presented for liquid carbon adsorption processes, they can also give indications of the costs in relation with the process conditions for gas phase carbon adsorption.

Table 4: Costs of air stripping in combination with activated carbon adsorption or biofiltration

CASE	I	II
AIRSTRIPPING		
Investment costs	150,000.-	2,400,000.-
Depreciation and interest	22,500.-	360,000.-
Labor and maintenance	26,400.-	211,200.-
Energy costs: • air	12,000.-	100,000.-
• water	4,000.-	200,000.-
TOTAL ANNUAL COSTS FOR THE STRIPPING PROCESS	*Dfl 64,900.-*	*Dfl 871,200.-*
EMISSION CONTROL BY GAS-PHASE CARBON ADSORPTION		
Investment costs	60,000.-	510,000.-
Depreciation and interest	9,000.-	76,500.-
Labor and maintenance	13,200.-	105,600.-
Pump energy costs	6,000.-	50,000.-
Carbon replacement	60,000.- (5 times/year))	45,000.- (each five years)
Regeneration on-site (Dfl 0.50/kg)		10,000,000.-
TOTAL ANNUAL COSTS FOR GAS-PHASE CARBON ADSORPTION	*Dfl 88,200.-*	*Dfl 10,277,100.-*
TOTAL ANNUAL COSTS	Dfl 153,100.-	Dfl 11,148,300.-
Costs per m^3 of treated water	**Dfl 1.91**	**Dfl 2.79**
EMISSION CONTROL BY BIOFILTRATION		
Investment costs (incl. filter materials)	300,000.-	20,000,000.-
Depreciation and interest	45,000.-	3,000,000.-
Labor and maintenance	26,400.-	211,200.-
Pump energy costs	6,000.-	320,000.-
TOTAL ANNUAL COSTS FOR BIOFILTRATION	*Dfl 77,400.-*	*Dfl 3,531,200.-*
TOTAL ANNUAL COSTS	Dfl 142,300.-	Dfl 4,402,400.-
Costs per m^3 of treated water	**Dfl 1.78**	**Dfl 1.10**

Biofiltration has been developed only recently and data about this process are scarce. The estimated small-scale investment costs are Dfl 300,000.-, including biofilter materials and compost. These costs were calculated on the basis of estimations given by Nobel for systems operating in the same low concentration range [10]. From a more recent research study [9] a relation between the annual quantity of contaminants treated and the investment costs at higher concentrations was derived. On the basis of this relation, the investment costs for large-scale applications can be estimated to be about Dfl 20 million.

Résumé and comparison with literature data

With respect to the total operating costs in small-scale operations, the processes of biofiltration, gas-phase activated carbon adsorption and direct adsorption from the liquid phase are competitive (Dfl 1.78 - Dfl 1.97/m^3). For large scale operations a hybrid process of air stripping and gas phase activated carbon adsorption appears to be a profitable option (Dfl 2.79 compared to Dfl 5.32/m^3). due to the increased loading capacity of the carbon (10% vs. 5% in liquid phase carbon adsorption). In literature, technical data are available which show that in this process the carbon can be regenerated on site.

The technical feasibility of gas phase activated carbon adsorption therefore seems to be better than for liquid phase carbon adsorption.

In the high concentration range biofiltration seems to be even more profitable (Dfl 1.10/m^3) from an economic viewpoint. This latter process has, however, the disadvantage of very large space requirements (see appendix B).

Literature cost values based on actual ground water or waste water purification systems are difficult to obtain, because until recently only air stripping without aftertreatment has been applied. Typical cost values found in literature for the 'stand-alone' process of air stripping are \$ 0.04 - \$ 0.17/1000 gal (Dfl 0.02 - 0.09/m^3). From an environmental point of view an additional technique to treat the stripper off-gases is essential. Such a combination will increase the total operating costs substantially.

Byers [7] showed that on a technical scale a combination of air stripping and gas phase activated carbon adsorption could reduce the annual operating costs by a factor of two compared to direct adsorption from the liquid phase. This observation gives further confirmation of the feasibility of this hybrid process.

In the recovery of organic vapours from air, vapour permeation using membranes has shown to be competitive with gas phase activated carbon adsorption from an economic viewpoint. This membrane filtration process has proven its feasibility on a pilot plant scale. The first estimations give values ranging from Dfl 0.47 - 0.64/kg VOC [38-39]. It should be emphasized that these are only preliminary values obtained for relatively 'dry' vapours. More research should be carried out to determine the economic and technical feasibility of this membrane filtration process in combination with air stripping.

The presence of water in the air current is not detrimental in biofiltration processes. Water on the biofilter materials is even a strict condition for an effective degrading process. At present only preliminary costs for large scale VOC degrading by biofiltration are available. For large scale processes the first estimations give values of Dfl 2.50/m^3 of treated water.

6.5.3 Investment and total operating costs for pervaporation based processes

In this section total investment and operating costs for pervaporation processes are given. A stand alone system is considered as well as a profitable hybrid system with activated carbon adsorption to establish higher rates of purification. Technical details on the pervaporation process which mainly refer to the composite membranes used and the space requirements are given in appendix C.

Table 5: Investment costs of a 400 m^2 pervaporation-unit (numbers in brackets for a spiral wound module)

Container	10,000.-	
Pumps	20,000.-	
16 membrane stacks @ Dfl 1,000.-/m^2 (Dfl 200.-/m^2)	400,000.-	(80,000.-)
4 vacuum vessels / condensers	65,000.-	
Sand filter / candle filter	15,000.-	
Panel	10,000.-	
Piping etc.	10,000.-	
Subtotal	**Dfl 530,000.-**	
Membrane costs (Dfl 100.-/m^2)	Dfl 40,000.-	
Total investment costs	**Dfl 570,000.-**	**(250,000.-)**

The costs for pervaporation have been determined on the basis of data provided by SETEC. This company supplies mobile pervaporation units with a total effective membrane area of 400 m^2. As pre-treatment techniques a sand filter and a candle filter are used. In table 5 the investment costs of a 400 m^2 pervaporation unit are specified. To give an indication of the effect of the module type on the investment costs both the price of a stainless steel module (Dfl 1,000.-/m^2) as well as a cheap spiral wound module (Dfl 200.-/m^2; membranes excluded) [23] are taken into account.

The cost calculations on the pervaporation system were performed with computer software developed by Blume [40]. These calculations are based on cross-flow equations by Weller and Steiner [41] and Pan and Habgood [42]. In this cross-flow model the feed flows parallel to the membrane surface, whereas the permeate is removed perpendicular to the membrane. It has been assumed that modules as described in this paper operate under these conditions. In this model a flux factor is defined which in general can express improvement of pervaporation performance due to the reduction of the membrane thickness, the use of other module types, increasing cross-flow rates and reduction of the downstream pressure.

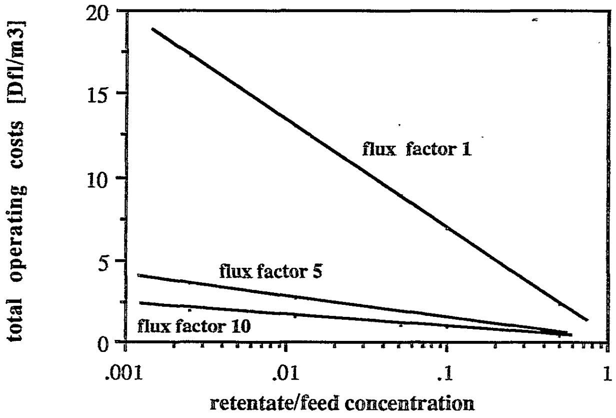

Figure 7: Total costs for pervaporation as a function of flux factor and recovery

In figure 7 the total small scale operating costs (standard investment costs: Dfl 570,000.-) for pervaporation are presented as a function of the flux factor and the ratio of retentate and influent concentration. A flux factor of 1 indicates that fluxes were taken as obtained in the results section for 110 μm membranes in plate and frame modules.

A flux factor of 10 indicates that fluxes are improved by a factor of 10. As was shown previously [16] for PDMS membranes a reduction of membrane thickness will have only a minor effect on the flux of the organic component. The component fluxes as they are presented in the results section can therefore only be improved by optimization of the three process parameters:

- *module type*
- *cross-flow velocity*
- *downstream pressure.*

This flux improvement factor has a considerable effect on the costs of the pervaporation process. In the following cost calculations a flux factor of 10 has been assumed on the basis of higher fluxes obtained with other modules [22, 23]. However, for some applications of pervaporation, especially in the low concentration range, this assumption may be to optimistic, due to strongly diminished driving forces.

Table 6: Costs for pervaporation (numbers in brackets for a spiral wound module)

CASE	**I**		**II**	
Investment costs	570,000.-	(250,000.-)	28,500,000.-	(12,500,000.-)
Depreciation and interest	85,500.-	(37,500.-)	4,275,000.-	(1,875,000.-)
Labor and maintenance	26,400.-		211,200.-	
Membrane replacement (three years)	13,300.-		670,000.-	
Energy costs:				
• liquid feed pump	2,000.-		100,000.-	
• vacuum pump	5,000.-		250,000.-	
• condensation	480.-		80,000.-	
TOTAL ANNUAL COSTS	Dfl 132,680.-	(Dfl 84,680.-)	Dfl 5,586,200.-	(Dfl 3,186,200.-)
Costs per m^3 of treated water	**Dfl 1.66**	**(Dfl 1.06)**	**Dfl 1.40**	**(Dfl 0.80)**

The annual costs for pervaporation are determined predominantly by the relatively high investment costs. The other most important operating costs are labour (2 hours per day) and the replacement of membranes each three years. The energy costs in pervaporation are determined by:

- feed pump
- vacuum pump
- condensation of the permeate.

The contributions to the energy costs of the vacuum pump and feed recycle pump can be determined easily from their power requirements. Cooling down to a temperature of - 20 °C would require a special cryo-unit. The refrigeration costs were assumed at Dfl 0.05 per kg of condensed permeate. For the silicone rubber membranes used in this study the total permeate flux (mainly water) through 10 µm membranes can be estimated at 130 g/m^2-h [16] at 99 % recovery. This would imply that on an annual basis using 20,000 m^2 of membrane area the costs for the energy required to condensate the permeate are Dfl 1,040,000.-. Applying the highly selective EPDM membranes investigated previously [18] instead of the less selective PDMS membranes, the flux of the organic component is not altered very much, whereas the water flux decreases substantially. For composite membranes with a 10 µm permselective layer of EPDM (ethylene propylene terpolymer) the water flux is reduced to 3 g/m^2-h. It can be calculated now that the annual cooling costs are reduced by over one order of magnitude to Dfl 80,000.- for this type of membranes.

> *The cost calculations show that pervaporation is an attractive alternative to the conventional processes from an economic point of view. The total annual operating costs are in the range of Dfl 0.80 - Dfl 1.66/m^3, depending on the scale of the process and applied module type.*

For small scale installations the total annual costs can be reduced by a factor of 1.5-2.0 in comparison with alternative processes. For large scale operations an even more profitable situation exists. The process can compete with biofiltration from an economic point of view, but in comparison with liquid phase carbon adsorption and gas phase carbon adsorption the total annual operating costs can be reduced considerably, from 13,5 MDfl in gas phase adsorption to 3 MDfl in pervaporation.

Pervaporation including emission control

The costs specified in table 6 have been obtained on the basis of 99% product recovery, which implies that the influent concentrations of respectively 10 g/m^3 and 500 g/m^3 will be reduced to 0.1 and 5 g/m^3. The steadily decreasing concentration in the module can have a drastic effect on the driving force for transport of the organic component.

If the downstream pressure deviates from zero, required membrane areas will increase drastically in order to establish a dictated recovery rate in the low influent concentration range.

Furthermore often very low effluent concentrations are required. A flux improvement factor of 10 may be rather optimistic in such cases. As a result the total operating costs will increase substantially.

In such cases pervaporation alone seems to be a less attractive option. With respect to this, a combination of pervaporation and activated carbon adsorption seems to have good prospects. Pervaporation can remove the bulk of the contaminants, thus increasing the life-time of the carbon bed. This combined set-up will ensure, that very low effluent concentrations are established. The hybrid process, which can operate considerably more effectively and sometimes more economically, is schematically represented in figure 8.

In table 7 the costs for the hybrid process are specified for a flux factor of 10 and an overall product recovery of 99.9 %, whereas the pervaporation now is assumed to operate at 90 % product recovery. This implies that only half of the membrane area is required compared to the cost calculation in table 6, thus reducing the investment costs by approximately the same factor.

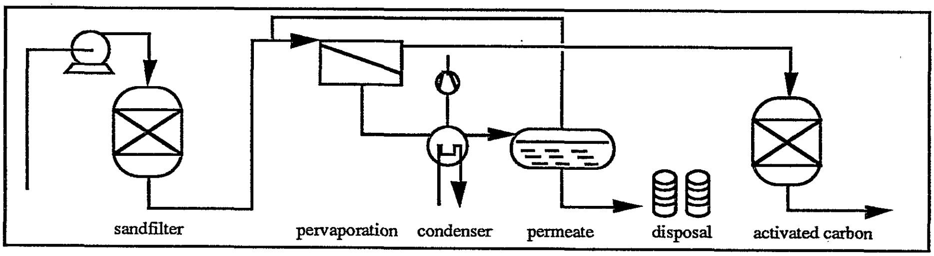

Figure 8: Schematic representation of the combined system set-up using pervaporation and liquid phase carbon adsorption

The data clearly indicate, that combination of pervaporation and liquid-phase carbon adsorption offers very interesting perspectives. A ten fold reduction of the concentrations in the effluent waste water can be established against a negligible increase in total operating costs for the small scale operations. For the large scale purifications the costs increase with a factor 1.5 compared to 99% recovery rate established with pervaporation only. However, the total operating costs are still smaller than in liquid phase carbon adsorption alone or air stripping/gas phase carbon adsorption processes. In cases where even higher recovery rates are dictated a pervaporation unit operating at 90 % product recovery and two carbon adsorbers in series with dimensions as given above can in principle reduce the influent concentration from 500 g/m^3 to 0.005 g/m^3 in the effluent.

Table 7: Costs for the combined pervaporation/carbon adsorption system set-up (brackets indicate spiral wound modules)

CASE	I		II	
Investment costs	Dfl 285,000.-	(125,000.-)	14,250,000.-	(6,250,00.-)
Depreciation and interest	42,750.-	(18,750.-)	2,137,500.-	(937,500.-)
Labor and maintenance	26,400.-		211,200.-	
Membrane replacement (three years)	6,650.-		335,000.-	
Energy costs: ◦ liquid feed pump	2,000.-		100,000.-	
• vacuum pump	2,500.-		125,000.-	
• condensation	240.-		40,000.-	
TOTAL ANNUAL COSTS FOR PERVAPORATION				
	Dfl 80,540.-	(Dfl 56,540.-)	Dfl 2,948,700.-	(Dfl 1,748,700.-)
<u>EMISSION CONTROL BY LIQUID-PHASE CARBON ADSORPTION</u>				
Depreciation and interest	9,000.-		255,000.-	
Labor and maintenance	13,200.-		105,600.-	
Energy costs	1,000.-		50,000.-	
Regeneration on-site			2,000,000.-	
Carbon replacement	12,000.-		720,000.-	
TOTAL ANNUAL COSTS LIQUID PHASE CARBON ADSORPTION				
	Dfl 35,200.-		Dfl 3,130,600.-	
TOTAL ANNUAL COSTS	Dfl 115,740.-	(Dfl 91,740.-)	Dfl 6,079,300.-	(Dfl 4,879,300.-)
Costs per m^3 of treated water	**Dfl 1.45**	**(Dfl 1.15)**	**Dfl 1.52**	**(Dfl 1.22)**

Comparison with literature data

Actual data on the removal of volatile organic components from waste water by pervaporation on a technical scale are not available yet. Pilot-plant studies have been performed by several investigators. Blume et al [23] determined the pervaporation performance of spiral-wound modules and carried out an economic evaluation of the process. For a system treating 16 m^3/h of contaminated water they came up with a value for the annual operating costs of \$2.36/1,000 gal (Dfl 1.24/m^3) at a recovery of 90%. Côté and Lipski [24] developed a micro computer program and investigated systematically the role of several parameters on the economics of the pervaporation process. The optimal operating conditions for respectively a module consisting of small and large hollow fibres as well as a spiral-wound module have been determined. For a system treating 10 m^3/h of contaminated water at an influent concentration of 10 g/m^3, a spiral-wound module should be preferred and removes 99 % of the contaminants at a price of \$ 0.79/m^3 (Dfl 1.58/m^3). Rautenbach and coworkers [43] proposed a different system for the recovery of solvent mixtures from aqueous solutions. A hybrid system consisting of a reverse osmosis unit, a water selective pervaporation process and two phase separators is applied to treat the stripper gases produced in regenerating a carbon bed. The costs for the treatment of 1 m^3 of desorbate water is DM 17.- (Dfl 19.30), including recycling of the recovered solvent. This indicates that a single phase separator and a pervaporation process using organophilic membranes will remove the volatile organic components from the desorbate water at considerably lower costs.

6.5.4 Final discussion

The economic and technical feasibility of different techniques for removing volatile organic components from aqueous solutions has been evaluated. In the sections above and with the help of the technical data summarized in the appendices the quantitative as well as some of the non quantitative 'consequences' of choosing the best alternative solution have been presented. In the tables below the final results are summarized.

The results of the economic evaluation are given in table 8. Again it should be emphasized that the cost considerations presented in the previous sections merely aim to give rough indications rather than exact estimates. However, the economic evaluation shows that in the very low concentration range (< 10 g/m^3; considered in case I) the liquid phase carbon adsorption process seems to be the cheapest option available. For similar product recovery rates pervaporation is far more expensive, whereas air stripping from an environmental point of view can only be applied in combination with either a gas phase carbon adsorption process or biofiltration, which increases the capital costs of the process considerably. In this concentration range the total operating costs are mainly determined by the depreciation and the labour costs. At higher influent concentrations the costs for replacement and/or regeneration will be of increasing importance. The liquid phase carbon adsorption process will than show out to be a less attractive option from an economic point of view.

Table 8: Total operating costs (in Dfl/m^3) for the processes considered (numbers in brackets indicate spiral wound modules)

CASE	I	II	RECOVERY
liquid phase carbon adsorption	1.97	5.32	99%
air stripping/gas phase adsorption	1.91	2.79	99%
air stripping/biofiltration	1.78	1.10	99%
pervaporation	1.66 (1.06)	1.40 (0.80)	99%
pervaporation/liquid phase carbon adsorption	1.45 (1.15)	1.52 (1.22)	99.9%
pervaporation/liquid phase carbon adsorption	1.78 (1.49)	1.86 (1.56)	99.999%

For moderate concentrations the three processes are competitive. The lowest total operating costs are obtained for an hybrid process of pervaporation and liquid phase activated carbon adsorption operating at 99.9% product recovery.

In high concentration operations pervaporation seems to supply a suitable process. Activated carbon adsorption processes are expensive due to the high costs for regeneration, whereas for biofiltration processes extremely large amounts of biofilter materials are required. This latter important process parameter (space requirements) and its values for the different processes are given in table 9.

This table shows that with respect to space requirements a pervaporation process will be preferred. This condition is especially important with respect to case II. A possible application of pervaporation would reduce the space required with a factor of 6 to 12 compared to activated carbon processes. A biofiltration system is practically excluded due to extremely large amount biofilter materials needed. In order to increase the product recoveries in case II an increase in membrane area will probably be preferred above the installation of a carbon adsorption unit.

Table 9: Estimated total space requirements of the different processes (m^3)

CASE	I	II	RECOVERY
liquid phase carbon adsorption	3.5	250	99%
air stripping/gas phase adsorption	7	600	99%
air stripping/biofiltration	10	20,000	99%
pervaporation	0.8	40	99%
pervaporation/liquid phase carbon adsorption	4.1	290	99.9%
pervaporation/liquid phase carbon adsorption	7.8	540	99.999%

Besides the considerations summarized in table 8 and 9 several other aspects will play a role in the decision about the most suitable process, like the kind of contaminants that can be removed, the quality of the effluent, the purity of the residue (recovered VOC), the ability of handling higher influent concentrations, the simplicity of the process, the support facilities required and the safety of the process. For the small scale project no clear distinction between the different processes could be made. For large scale operations, however, one is intended to use pervaporation, mainly because this process can handle higher influent concentrations quite easily. The VOC's are obtained as an almost pure liquid, the process is simple, whereas only minor support facilities are required.

6.6 CONCLUSIONS

Cost calculations are given for various processes for which several basic assumptions and conditions have been evaluated. The most important ones are the carbon loading capacity and the carbon regeneration costs for the activated carbon adsorption and the flux improvement factor for the pervaporation process.

Assuming a flux improvement factor of 10, it is concluded that in the moderate (and higher) concentration range, pervaporation is the best technique, both from an economic as well as from a technical point of view. For low concentrations activated carbon processes are the best choice. When non toxic, non volatile organic components are present an air stripping process has good prospects to remove small amounts of solutes. To prevent that a water pollution problem is transferred to an air pollution problem, a second technique should be used to treat the stripper off-gases. Both gas phase activated carbon adsorption and biofiltration show interesting possibilities.

The biofiltration process is not very efficient for treating very large quantities of polluting substances, because of the rapidly increasing amount of biofilter materials required. With respect to the space requirements, the pervaporation process is by far the best option available.

Special attention should be paid to a combination of pervaporation and activated carbon adsorption. Pervaporation removes the largest quantity of VOC's present, whereas activated carbon can reduce the effluent concentrations to very low values. Therefore a hybrid process is very attractive, because several organic substances will be removed and high product recoveries can be established at relatively low cost.

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6.8 APPENDICES

APPENDIX A: LIQUID PHASE ACTIVATED CARBON ADSORPTION

In this appendix the technical details are given, which have been used to estimate the investment costs and the total operating costs of the liquid phase carbon adsorption process. These details can be divided in two categories:

- systems design
- regeneration.

System design

The most important factor in dimensioning the carbon adsorber is the contact time of the contaminated water and the carbon granulate. For a 3.5 m^3 adsorber the filtration velocity was 1.4 mm/s, implicating a contact time of approximately 18 minutes, which seems to be an adequate value [2]. On the basis of this contact time, a system can be designed to treat 500 m^3/h of waste water. Literature data are available on adsorbers with a diameter of 3 m and a bed height of 2.5 m. A contact time of 20 minutes would in this case indicate a filtration velocity of 2 mm/s. This would require 10 adsorbers with a total volume of 250 m^3 and a load of 90,000 kg.

Regeneration

Regeneration costs were a very uncertain factor in determining the total operating costs. The most simple case is a feed with a very low amount of polluting organic substances. The total operating costs can be calculated provided that the loading capacity of the activated carbon is known. After bed break through is observed the filter material is replaced and the process can be restarted. This seems to be the best option available as long as the loading period is at least one month [2].

For large scale/high concentration applications regeneration off-site has not been considered, because very unrealistic circumstances have to be dealt with. Each year 40 million kg carbon (5,000 kg/hour) at a price of Dfl 2.-/kg carbon (Dfl 20.-/1,000 m^3 water treated) has to be regenerated. This implies that adsorbers have to be cleared out and refilled continuously, which is not a very practical situation.

The applicability of regeneration in liquid phase activated carbon adsorption in general and in this case (II) in particular can also be questioned, because not only toxic compounds will be present in the waste water, but also substances which in principle can be drained directly. Furthermore compounds of high molecular weight will be adsorbed, which will not desorb readily from the carbon surface at temperatures slightly higher than 100 °C. This poor selectivity of the activated carbon diminishes the efficiency of the adsorption process to a considerable extent. It should be emphasized that this a very important point which is detrimental to liquid phase activated carbon adsorption and therefore often other processes will be preferred. Still, calculations have been performed, although field experience concerning the on-site regeneration of liquid phase adsorbed carbon is not available in the literature and the exact composition of the waste water is not known.

APPENDIX B: AIR STRIPPING

With respect to environmental considerations air stripping is not very attractive, because the pollution is transferred from the aqueous phase to the vapour phase. A combination with a second technique in series is therefore essential to treat stripper off-gases. This aftertreatment can be performed in two different ways:

- activated carbon adsorption
- biofiltration.

In this appendix the specific problems of combining airstripping with an emission control unit and the details in the design of the hybrid processes will be presented.

Emission control

Activated carbon adsorption is only effective when the off-gases are not saturated with water. In the latter case water will condense on the carbon. For practical applications the temperature of the air stream from the air stripper has to be raised a few degrees to decrease the relative humidity to values less than 50% [6, 7]. The advantage over liquid phase activated carbon adsorption is the increased loading capacity. Furthermore poisoning of the carbon-bed by nonvolatile high molecular weight components is prevented. The air stripping process, therefore, earns itself back by reducing the number of regenerations and by increasing the carbon life time.

For the posttreatment of the stripped off-gases a biofiltration process seems to be more adequate. The humidity of the filter is an essential condition and therefore the off-gases do not have to be heated. Degrading of the organic components takes place in a stagnant aqueous liquid film, built upon the compost particles. Problems, however, occur in the degradation of chlorinated hydrocarbons. Free chlorine molecules, created in the degrading process, poison very slowly the biofilter. Future developments aim to keep the biomass in good condition by rinsing out chlorine atoms by means of a trickling process [11]. This means further rise of treatment costs whereas the question arises if it will be allowed to drain the chlorinated trickling water without further treatment.

System design

The number of adsorbers is determined on the basis of the required filtration velocity, with 0.25 m/s being a good average value [6, 7, 8]. For large scale applications three strippers are in operation, producing totally 10,000 m^3 off-gases per hour. Using the carbon adsorbers with dimensions as described above this would imply that 3 adsorbers in parallel are required of which two are in operation, whereas the third one has to be regenerated. To reduce the influent concentration to values below 5 g/m^3 the dimensions of the three stripper columns are given below (the dimensions of the small stripper column are given in brackets):

- diameter: 3 (0.75) meter
- height: 26 (8) meter

The total volume of this large-scale installation is 600 m^3.

The feed flow rate in the small-scale stripper was about 8.3 m^3/hr and the air current 2,000 m^3/hr. A small-scale carbon adsorber unit is used as described in the previous appendix. Under these circumstances the concentrations in the influent are reduced from 5,000 - 18,000 µg/l to less than 3 µg/l in the effluent. The space required for this installation is 7 m^3.

Emission control by biofiltration processes requires a lot more space compared to alternative processes. Assuming a degrading velocity of 15 g/m^3-h the biofilter in the small-scale installation would be 10 m^3 in size and for the large-scale process 20,000 m^3 are required. This will practically exclude biofiltration processes for large scale/high concentration applications.

APPENDIX C: PERVAPORATION

Membranes are very well known for their space saving properties. To what extent this is the case in the removal of volatile organic components from water is discussed in this appendix. Furthermore attention will be paid to the resistance-in-series model which was explored elsewhere to determine the effects of membrane thickness and of flow conditions on the pervaporation performance.

Resistance-in-series model

The membranes used in our scale-up experiments were of the dense homogeneous type and had an average effective thickness of approximately 110 µm. For practical applications a selective layer is deposited on a support material. The support is in most instances a porous micro- or ultrafiltration membrane. The structure of these thin film composite membranes is shown in the figure below. In principle the permselective toplayer material can be any of the elastomers studied previously [18]. In the economic evaluation it will be this type of composite membranes that will be taken for accounting purposes. The thickness of the actual separating layer has to be optimized both with respect to the organic component flux and to the selectivity in the pervaporation process.

From the resistance-in-series model [16] the effective membrane thickness of the membrane with the highest selectivity observed [18] can be estimated. On the basis of literature data [23-24] a liquid boundary layer mass transfer coefficient (k_L) of 3.10^{-5} m/s has been assumed. The membrane should now be adapted to that k_L-value. When the overall resistance is determined exclusively by the liquid boundary layer resistance the organic component flux (J_{OC}) will be 27 g/m^2-h for a 250 g/m^3 toluene concentration. Suppose that a 10% flux decrease (24g/m^2-h) due to a finite membrane resistance is still acceptable. With the resistance-in-series model the effective membrane thickness of an EPDM membrane (having the highest selectivity factor) can now be calculated.

$$J_{oc} = k_{OV} * \text{concentration}$$

$$\frac{1}{k_{OV}} = \frac{1}{k_L} + \frac{\ell}{\mathcal{P}}$$

The permeability coefficient ($\mathcal{P}$) for toluene in EPDM membranes is $1.1*10^{-9}$ m^2/s. From the given equations the required effective membrane thickness can be estimated at ~ 8 μm. So the basic approach is not the reduction of the effective membrane thickness, but rather adaption of the effective membrane thickness to an established boundary layer mass transfer coefficient.

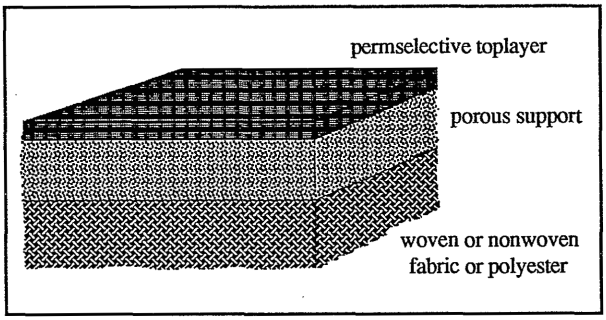

Figure 8: Schematic structure of a thin-film composite membrane

Process design

With respect to the space limitations on oil platforms pervaporation seems to be the best option available. For the plate-and-frame module used in our experiments a value of 250 m^2/m^3 for the ratio of membrane area and required space can be calculated. Typical values for spiral-wound and hollow fiber modules are 500 and 1000 m^2/m^3 respectively. Taking an average value of 500 m^2/m^3 the space required for small scale operations is 0.8 m^3 and for the large scale process 40 m^3. This gives a reduction with a factor 5 - 10 in comparison to alternative processes.

SUMMARY

Volatile organic hydrocarbons in ground water, surface water or waste water are a continuous threat to the public health. Often traditional purification techniques cannot be applied to remove these components from aqueous solutions. In this thesis the technical and economic feasibility of pervaporation, a rapidly developing membrane filtration technique, will be investigated for the removal of trace organics from water.

At present two basic techniques are available, viz.:

- adsorption onto activated carbon
- air stripping.

Activated carbon adsorption processes have already proven to be successful in several cases. The technique is based on the interaction of the component to be removed and the surface of the carbon particles. After the complete surface is occupied, the carbon has to be regenerated. The costs of this process depend on the kind of pollutant, adsorption system and regeneration technique.

Air stripping processes are based on the volatility of the hydrocarbons. Air or steam is brought in contact with the contaminated water to remove the volatile pollutant. To prevent that a water pollution problem is transferred to an air pollution problem the off-gases have to be treated afterwards. For this purpose several options are available of which gas-phase adsorption onto activated carbon and biofiltration have proven to be the most promising.

In pervaporation a liquid mixture is brought in contact with a membrane at the upstream side, whereas the permeate is removed as a vapour at the downstream side. This is established by reducing the relative vapour pressure at the permeate side through either the use of an inert carrier gas or an applied vacuum. The permeate is successively obtained in a condenser. In the pervaporation of trace organics from water the pollutants are obtained as an almost pure liquid, whereas no additional substances (like activated carbon or micro-organisms) are required.

In this particular application of pervaporation diffusion limitations of the organic component in the feed solution play an essential role. Therefore a resistance-in-series model is used in chapter 2 to describe the pervaporation performance of elastomeric membranes in the removal of volatile organic components from water. Membranes with a wide range of thicknesses have been prepared

and the pervaporation behaviour for the removal of toluene and trichloroethylene from aqueous solutions has been studied. Mass transfer coefficients in the liquid boundary layer and in the membrane respectively have been determined. The experiments show that the hydrodynamic boundary layer resistance is of great importance. In chapter 3 the influence of the hydrodynamic resistance on the removal of toluene and trichloroethylene from binary aqueous solutions by pervaporation has been studied more extensively. Mass transfer coefficients have been determined for laminar flow in a flat channel cell as well as laminar and turbulent flow in a stirred cell. Liquid boundary layer mass transfer coefficients follow from Sherwood relations. Reasonable accurate predictions of the overall mass transfer coefficient in the pervaporation process were observed.

In chapter 4 more fundamental aspects of the pervaporation process have been studied. A wide range of homogeneous elastomeric membranes have been prepared using dicumylperoxide as a general crosslinking agent. Pervaporation experiments have been performed under identical hydrodynamic conditions in order to fix the boundary layer mass transfer coefficient at a constant and known value. For comparison of the permeabilities of different pervaporation membrane materials this is of utmost importance. A wide range of selectivity factors is obtained.

The permeability data obtained for the various elastomers have been related to the chemical and physical nature of the elastomers through the solubility parameter approach and the glass transition temperature respectively. Both diffusional and sorption effects seem to be important, determining the water transport behaviour in the elastomeric membranes. Differences in the permeabilities of the organic component can primarily be ascribed to structural parameters, like degree of unsaturation and presence of steric side groups.

Preferential sorption in elastomeric membranes is generally considered as the most essential step in the pervaporation process. Therefore the sorption behaviour of elastomeric membranes for the removal of volatile organic components from water in aqueous solutions of toluene and trichloroethylene is studied in chapter 5. Flory-Huggins thermodynamics are applied to describe and predict the sorption behaviour of pervaporation membranes in a more quantitative way. Polymer/liquid interaction parameters are obtained from swelling experiments, whereas the liquid/liquid interaction parameter is calculated from the simple binary Flory-Huggins equations and the solubility of the organic component in water. The thus obtained binary interaction parameters are used in ternary Flory-Huggins equations to describe with reasonable good accuracy the sorption behaviour of the aqueous solutions. A "Henry-type" of sorption behaviour of the organic component may be assumed in the low concentration range.

In chapter 6 the different processes have been compared from an accounting point of view on the basis of two potential applications. In the first case a small-scale process is considered, typical for ground water sanitation. The second case is dealing with a large-scale waste water purification system, typical for industrial waste water treatment. The evaluation has been carried out for single processes as well as for hybrid systems.

Besides the attractiveness from a technical point of view, the pervaporation process shows also good prospects from an economic point of view.

SAMENVATTING

Vluchtige organische koolwaterstoffen in grondwater, oppervlaktewater of afvalwater zijn een continue bedreiging voor de volksgezondheid. Vaak kunnen traditionele technieken niet worden toegepast om deze stoffen uit waterige oplossingen te verwijderen. In dit proefschrift zal de technische en economische haalbaarheid van pervaporatie, een zich snel ontwikkelende membraanfiltratietechniek, worden onderzocht voor de verwijdering van organische microverontreinigingen uit water. Op dit moment zijn twee basistechnieken beschikbaar, te weten:

- adsorptie op actieve kool
- luchtstrippen.

In verschillende gevallen zijn actief kool adsorptieprocessen al met succes toegepast. Het principe van deze techniek berust op de affiniteit van de te verwijderen component met het oppervlak van de kooldeeltjes. Op het moment dat het volledige oppervlak bezet is, dient de kool te worden gereactiveerd of vervangen. De kosten voor het regeneratieproces kunnen hoog zijn, afhankelijk van de soort geadsorbeerde verontreinigingen, het adsorptiesysteem en de regeneratietechniek.

Luchtstripprocessen zijn gebaseerd op de vluchtigheid van de koolwaterstoffen. Lucht of stoom wordt in contact gebracht met het verontreinigde water om de vluchige component te verwijderen. Om te voorkomen dat het verontreingingsprobleem zich verplaatst van de waterfase naar de luchtfase zullen de afgassen moeten worden nabehandeld. Hiervoor bestaan verschillende mogelijkheden, waarvan adsorptie op actieve kool vanuit de gasfase en biofiltratie het meest veelbelovend lijken te zijn.

Bij pervaporatie wordt een vloeistofmengsel in contact gebracht met het membraan aan de voedingszijde, terwijl het permeaat als damp aan de permeaatzijde wordt afgevoerd. Dit wordt bewerkstelligd door de relatieve dampspanning aan de permeaatzijde te verlagen door het gebruik van een een inert dragergas of het aanbrengen van een vacuüm. Het permeaat wordt vervolgens als vloeistof in een condensor opgevangen. Op deze manier worden, bij pervaporatie van organische microverontreinigingen uit water, de koolwaterstoffen als bijna zuivere vloeistof verkregen, terwijl geen additionele stoffen (zoals actief kool, micro-organismen of compost) nodig zijn.

Bij deze toepassing van pervaporatie spelen diffusielimiteringen van de organische component in de voedingstroom een grote rol. Daarom wordt in hoofdstuk 2 een weerstanden-in-serie model gebruikt om het pervaporatiegedrag van elastomere membranen bij de verwijdering van vluchtige organische stoffen uit water te beschrijven. Membranen met verschillende diktes werden bereid en het pervaporatiegedrag voor de verwijdering van trichlooretheen en tolueen uit waterige oplossingen werd bestudeerd. Stofoverdrachtscoefficienten in de grenslaag en in het membraan werden bepaald. De experimenten tonen aan dat de hydrodynamische grenslaagweerstand van groot belang is. In hoofdstuk 3 wordt de invloed van de hydrodynamische weerstand op de verwijdering van tolueen en trichlooretheen uit binaire waterige oplossingen met behulp van een pervaporatieproces verder onderzocht. Stofoverdrachtscoefficienten werden bepaald voor zowel laminaire stroming in een vlakke cel, als voor laminaire en turbulente stroming in een geroerde cel. Sherwood correlaties werden gebruikt om grenslaag-stofoverdrachtscoefficienten te berekenen. De totale stofoverdrachtscoefficient in het pervaporatieproces kon met voldoende zekerheid worden voorspeld.

In hoofdstuk 4 komen meer fundamentele aspecten van het pervaporatieproces aan de orde. Een groot aantal homogene elastomere membranen werd bereid. Pervaporatie-experimenten werden uitgevoerd, bij identieke hydrodynamische stromingscondities om zodoende de grenslaag-stofoverdrachtscoefficient op een vaste en constante waarde te fixeren. Voor een vergelijking van de permeabiliteiten van verschillende pervaporatiemembranen is dit van groot belang. De selectiviteit van de membranen bleek onderling sterk te verschillen.

De permeabiliteiten die werden verkregen voor de verschillende elastomeren werden gerelateerd aan de fysische en chemische eigenschappen van de elastomeren door middel van de oplosbaarheidsparametertheorie en de glasovergangstemperatuur. Zowel diffusie- als oplosbaarheidseffecten lijken belangrijk te zijn bij het watertransport in elastomere membranen. Verschillen in permeabiliteit van de organische component kunnen voornamelijk worden toegeschreven aan structuurkenmerken, zoals de mate van onverzadigdheid en de aanwezigheid van sterische zijgroepen.

Preferentiële sorptie in elastomere membranen wordt in het algemeen gezien als de meest essentiële stap in het pervaporatieproces. Daarom is het sorptiegedrag van elastomere membranen bij de verwijdering van vluchtige organische componenten uit binaire waterige oplossingen van tolueen en trichlooretheen bestudeerd in hoofdstuk 5. Flory-Huggins thermodynamica werd toegepast om het sorptiegedrag van pervaporatiemembranen te beschrijven en te voorspellen op een kwantitatieve manier. Polymeer/vloeistof interactieparameters werden verkregen uit zwelexperimenten, terwijl de vloeistof/vloeistof interactieparameter werd berekend uit eenvoudige binaire Flory-Huggins vergelijkingen en de oplosbaarheid van de organische component in water. De aldus verkregen binaire interactieparameters zijn gebruikt in ternaire Flory-Huggins vergelijkingen om redelijk succesvol het sorptiegedrag in waterige oplossingen te beschrijven. Een "Henry-achtig" sorptiegedrag van de organische component mag alleen in het lage concentratiegebied worden aangenomen.

In hoofdstuk 6 worden de verschillende processen voor het verwijderen van vluchtige organische stoffen uit water met elkaar vergeleken vanuit kostenoogpunt voor twee potentiele toepassingen. In het eerste geval wordt een kleinschalig proces bestudeerd, dat representatief is voor grondwatersaneringen. In het tweede geval wordt gekeken naar een grootschalig afvalwater-zuiveringssysteem, representatief voor de behandeling van industrieel afvalwater. De evaluatie werd uitgevoerd voor zowel enkelvoudige systemen als hybride processen.

Naast de aantrekkelijkheid vanuit technisch oogpunt blijkt het pervaporatieproces ook door economische redenenen goede perspectieven te bieden.

SAMENVATTING VOOR DE LEEK

In Nederland zijn tal van plaatsen bekend waar de bodem sterk verontreinigd is. Membranen lijken in het algemeen interessante mogelijkheden te bieden bij het oplossen van milieuproblemen. Voor de verwijdering van aromatische (tolueen, benzeen) of gehalogeneerde koolwaterstoffen (trichlooretheen, tetrachlooretheen) uit waterige oplossingen lijkt pervaporatie goede perspectieven te bieden. Het doel van dit onderzoek is de ontwikkeling van een pervaporatiemembraan voor de verwijdering van vluchtige organische stoffen uit grondwater, oppervlaktewater of industrieel afvalwater.

Pervaporatie is een zich snel ontwikkelende, relatief nieuwe membraanfiltratietechniek. Bij het pervaporatieproces wordt het 'vervuilde' water aan de voedingszijde in contact gebracht met het membraan, terwijl aan de andere kant -de permeaatzijde- een vacuüm wordt aangelegd. Hierdoor ontstaat een concentratieverschil, met als gevolg dat met name de organische deeltjes zich van de voedingszijde naar de permeaatzijde bewegen. De membranen die bij deze techniek gebruikt worden zijn niet poreus, in tegenstelling tot traditionele membranen. De scheiding vindt dan ook niet plaats op basis van verschillen in deeltjesgrootte, maar op basis van verschillen in oplosbaarheid en beweeglijkheid van de te scheiden deeltjes in het membraan. Voor commerciële doeleinden moeten de membranen dunner zijn dan ééntiende millimeter. In veel gevallen worden echter nog kleinere diktes gewenst. In principe kunnen deze membranen gemaakt worden, maar ze hebben vaak een geringe mechanische sterkte. Dit is de reden waarom gebruik wordt gemaakt van zogenaamde composiet membranen. Een dunne niet-poreuze toplaag wordt aangebracht op een poreuze onderlaag. De toplaag is de selectieve laag die verantwoordelijk is voor de scheidende eigenschappen. De poreuze laag dient slechts ter ondersteuning van de dunne selectieve toplaag en heeft zelf een te verwaarlozen effect op de scheiding.

Belangrijke procesparameters bij de beschrijving van het pervaporatieproces zijn de dikte van het membraan (de selectieve toplaag) en de langstroomsnelheid aan het vloeistof/membraan grensvlak. Deze twee parameters zijn systematisch bestudeerd. Met betrekking tot het transport in het membraan is de oplosbaarheid van de deeltjes in het membraan onderzocht.

Tot slot is de toepasbaarheid van deze nieuwe waterzuiveringstechniek vanuit zowel technisch als vanuit economisch oogpunt vergeleken met alternatieve technieken, zoals actief koolfiltratie, luchtstrippen en biofiltratie.

LEVENSLOOP

Herry Nijhuis werd geboren op 7 september 1959, te Hengelo (O). In 1977 behaalde hij het Atheneum-B diploma aan de Openbare Scholengemeenschap Bataafse Kamp aldaar.

In datzelfde jaar begon hij de studie Chemische Technologie aan de toenmalige Technische Hogeschool Twente te Enschede. Hij behaalde in 1983 het baccalaureaatsdiploma (onderzoekgroep Chemische Gezondheidstechniek) en in 1985 het ingenieursdiploma (onderzoekgroep Biomedische Materiaaltechniek).

Op 1 september 1985 trad hij in dienst van de T.H. Twente als wetenschappelijk assistent in de onderzoekgroep 'Membraanfiltratie' van de vakgroep 'Macromoleculaire Chemie en Materiaalkunde' om het beschreven promotie-onderzoek uit te voeren. Vanaf 1 januari 1990 was hij bij dezelfde groep in dienst als medewerker onderzoek.

Vanaf 1 augustus 1990 is hij als wetenschappelijk onderzoeker belast met het onderzoek naar de ontwikkeling, modellering en toepassing van scheidingsprocessen bij het ATO, Agrotechnologisch Onderzoeksinstituut (afdeling: fysische be- en verwerking van voedsel en niet-voedselprodukten) te Wageningen.