

Selection of Elastomeric Membranes for the Removal of Volatile Organics from Water

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SYNOPSIS

A wide range of homogeneous elastomeric membranes has been prepared using dicumylperoxide as a general cross-linking agent. The membranes have been used for both equilibrium sorption measurements and steady-state pervaporation experiments to study solution-diffusion phenomena in the removal of volatile organic components from aqueous solutions. 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 up to a value of 100,000 are obtained, whereas usually the permeabilities for the organic component are in the range of 10^{-10} – 10^{-9} m²/s and 10^{-14} – 10^{-12} m²/s for water. The permeation and sorption 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 behavior in the elastomeric membranes. The solubility of the organic component appears to be independent of this combined solubility parameter. 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. © 1993 John Wiley & Sons, Inc.

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 into 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[™] (polyester), 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

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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 behavior 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 has been explained already qualitatively with a 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 in research on vapor recovery and treatment of aqueous solutions using this elastomer. There are, however, indications that other elastomers could have 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 top layer 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 a 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 toward the permeating organic component.
- A permselective top layer, 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 top layer, 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, results are discussed concerning the development of a thin selective top layer. For the preparation of homogeneous membranes, different elastomers are used in this paper and their pervaporation and sorption behavior have 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.

PROPERTIES OF ELASTOMERS

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 backbone structure.

For the backbone structure, important effects may stem from the

- type of atoms
- degree of saturation
- presence of aromatic or heterocyclic groups, and
- *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 backbone, 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.²⁰⁻²²

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 mobility 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 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 that 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.

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 agents²³:

- 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 Dienelike 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 h 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 2–5 min.

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 a proper steric relationship to permit rearrangements in the molecules as shown for accelerated sulfur vulcanization.

Several polyvalent organic compounds also have such sites and are used with unsaturated dienelike 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).

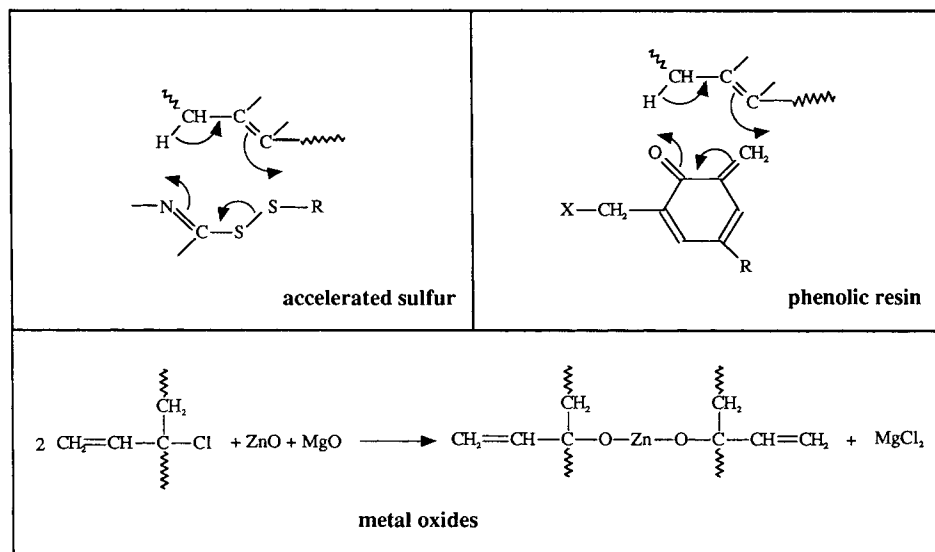


Figure 1 Schemes for some cross-linking procedures of dienelike elastomers.

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 dienelike 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 condensation²⁴ or a hydrosilylation reaction,²⁵ as indicated in Figure 2.

In the condensation reaction, a hydroxyl end-blocked polysiloxane is mixed with a polyfunctional organosilicate that 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.

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 hydrosilylation reaction described above or to 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 sulfur vulcanization is impossible, because of the absence of reactive double bonds. Ostromysslenski discovered already in 1915 the possibility of cross-linking natural rubber with benzoyl peroxide.²⁶ However, benzoyl peroxide vulcanizates have lower strength and poorer heat resistance than do sulfur vulcanizates. With the development of other peroxides in the 1950s 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.

Dicumylperoxide (DCP) has 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 nonvolatility 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 bulletin²⁷ and range from 6 to approximately 12 min at 155°C for the elastomers described in this paper. It can be calculated that after 7–10 half-lives in any peroxide system a plateau is reached. However, it is not necessary to cross-link such a long time. After 3–4 half-lives, mechanical properties, like tensile strength, modulus, and compression set, have attained about 90% of their ultimate value. Short cur-

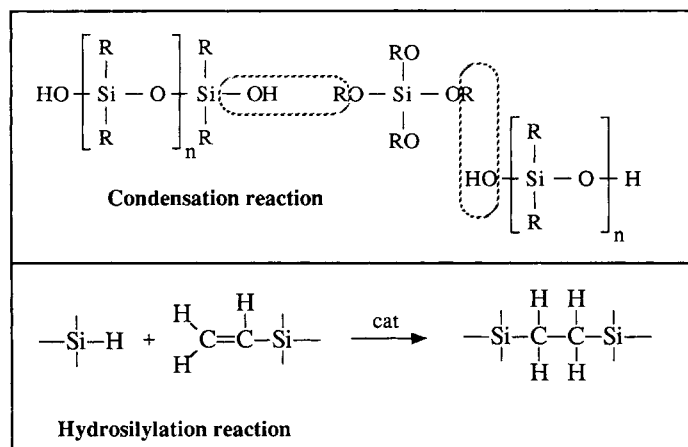


Figure 2 Silicone rubber room-temperature vulcanizing (RTV) systems.

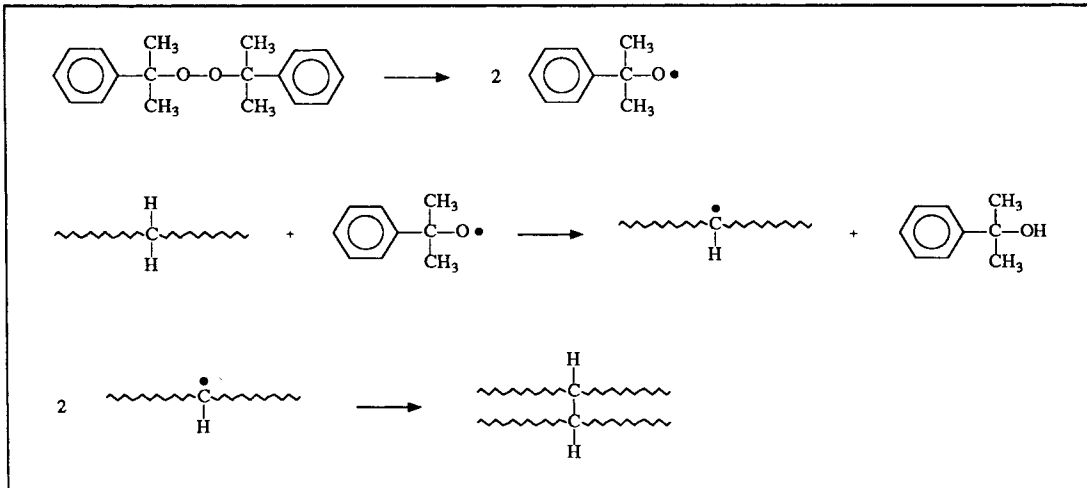


Figure 3 Peroxide vulcanization system.

ing cycles are often preferred, because of a resulting lower degree of polymer degradation that follows from small amounts of degradation initiating compounds that are always present.

Résumé

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

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

THEORY

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 behavior 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:

$$J_{oc} = k_{OV} \cdot \phi_{oc}^h \quad (1)$$

The overall mass transfer coefficient k_{OV} [m/s] can simply be determined from measurements of bulk feed concentration ϕ_{oc}^b [m³/m³] and steady-state permeate component flux in the pervaporation experiments J_{oc} [m³/m²·s]. 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 ($1/k_M = l/\mathcal{P}_{oc}$).

$$\frac{1}{k_{OV}} = \frac{1}{k_L} + \frac{1}{k_M} = \frac{1}{k_L} + \frac{1}{\mathcal{P}_{oc}} \quad (2)$$

In this equation, l [m] represents the effective membrane thickness, and \mathcal{P}_{oc} [m²/s], the permeability of the membrane for the organic component. The overall mass transfer coefficient k_{OV} [m/s] 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 eqs. (1) and (2).

The water flux J_w [$\text{m}^3/\text{m}^2\cdot\text{s}$] is not altered because of concentration polarization phenomena,¹⁸ which makes it possible to calculate the water permeability \mathcal{P}_w [m^2/s] according to eq. (3):

$$\mathcal{P}_w = J_w^p \cdot l \quad (3)$$

It is now also possible to calculate the so-called intrinsic pervaporation selectivity ($\alpha_{oc/w}^i$), which is the membrane selectivity in the hypothetical case that boundary layer effects could be excluded:

$$\alpha_{oc/w}^i = \frac{\mathcal{P}_{oc}}{\mathcal{P}_w} \quad (4)$$

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 behavior 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:

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

Since the swelling of a polymer in a solvent is connected with a relatively small increase in entropy ΔS_m [$\text{J}/\text{mol}\cdot\text{K}$], the magnitude of the enthalpy term ΔH_m [J/mol] is an important factor in determining the sign of the free-energy change ΔG_m [J/mol]: ΔH_m should be as low as possible. Hildebrand and Scott²⁹ proposed that

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

in which V_{mixt} [m^3/mol] represents the molar volume of the mixture, and ϕ_i and ϕ_j [m^3/m^3], the volume fractions of i and j , respectively, in the mixture. The expression $(\Delta E_i/V_i)$ is the energy of vaporization per cubic meter, which has been often described as the "internal pressure" or the "cohesive energy density" and it is related to the solubility parameter δ_i [$\text{J}^{1/2}/\text{mol}\cdot\text{K}$]:

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

The total energy of vaporization ΔE_i [J/mol] 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:

$$\Delta E_i = \Delta E_d + \Delta E_p + \Delta E_h \quad (8)$$

Combining eqs. (7) and (8) gives

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

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 .

Because of mutual interactions between the components of the liquid feed mixture, the solubility parameter approach is usually less successful for polymer samples in binary liquid mixtures. Still, for certain ternary 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 and Hoftijzer³³ gave the most extensive tabulations and subdivided 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.

EXPERIMENTAL

Materials

The polymers used in this study are listed in Table I, whereas the solvents (analytical grade) for dissolving the polymers and the cross-linking agent dicumylperoxide (DCP) were purchased from Merck and were used without further purification.

For homogenization of the demixed two-phase permeate, we used ethanol of analytical grade that was dried on molecular sieves. Water was deionized and ultrafiltrated before use.

Table I List of Elastomers Studied

Elastomer (product name)	Abbreviation	Membrane Thickness Used (μm)	Molecular Structure
Polybutadiene (Finaprene 250)	BR	50–150	$\begin{array}{c} \text{---H}_2\text{C} \quad \quad \text{H} \\ \quad \quad \quad \diagdown \quad \diagup \\ \quad \quad \quad \text{C}=\text{C} \\ \quad \quad \quad \diagup \quad \diagdown \\ \text{H} \quad \quad \quad \text{CH}_2\text{---} \end{array}$
Polychloroprene (Neoprene TW)	CR	50	$\begin{array}{c} \text{---H}_2\text{C} \quad \quad \text{H} \\ \quad \quad \quad \diagdown \quad \diagup \\ \quad \quad \quad \text{C}=\text{C} \\ \quad \quad \quad \diagup \quad \diagdown \\ \text{Cl} \quad \quad \quad \text{CH}_2\text{---} \end{array}$
Ethylene–propylene terpolymer (Keltan 578)	EPDM	40–200	$\begin{array}{c} \quad \quad \quad \\ \text{---C---C---C---C---} \\ \quad \quad \quad \\ \quad \quad \quad \quad \text{CH}_3 \end{array}$
Fluorocarbon elastomer (Viton [®] GF)	FKM	100	$\begin{array}{c} \text{H} \quad \text{F} \quad \quad \text{F} \quad \text{F} \\ \quad \quad \quad \quad \\ \text{---C---C---C---C---} \\ \quad \quad \quad \quad \\ \text{H} \quad \text{F} \quad \quad \text{F} \quad \text{CF}_3 \end{array}$
Polyoctenamer (Vestamer [®])	OT	140	$\text{---}(\text{CH}_2)_3\text{---CH=CH---}(\text{CH}_2)_3\text{---}$
Nitrile butadiene rubber (18, 28, 33 en 38% AN) (Perbunan 1807–3807)	NBR	120–160	$\begin{array}{c} \text{---H}_2\text{C} \quad \quad \text{H} \quad \quad \quad \quad \\ \quad \quad \quad \diagdown \quad \diagup \quad \quad \quad \quad \\ \quad \quad \quad \text{C}=\text{C} \quad \quad \quad \text{C---C---} \\ \quad \quad \quad \diagup \quad \diagdown \quad \quad \quad \quad \\ \text{H} \quad \quad \quad \text{CH}_2\text{---} \quad \quad \quad \text{C} \\ \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \\ \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \text{N} \end{array}$
Epichlorohydrin terpolymer (Hydrin 400)	ETER A	180	$\begin{array}{c} \text{---CH}_2\text{---CH---O---} \\ \quad \quad \quad \\ \quad \quad \quad \text{CH}_2\text{Cl} \end{array}$ <p>(polyepichlorohydrin)</p>
Polyurethane (Urepan 640)	AU	170	$\text{HO---P}_n\text{---C---C---NH---R---NH---C---O---P}_n\text{---OH}$ $\quad \quad \quad \quad \quad \quad $ $\quad \quad \quad \text{O} \quad \quad \quad \text{O}$
Polydimethylsiloxane (General Electric RTV 615)	PDMS	60–240	$\begin{array}{c} \text{CH}_3 \\ \\ \text{---Si---O---} \\ \\ \text{CH}_3 \end{array}$
Polyacrylate rubber (Hycar [®] 4051 EP)	ACM	140	$\begin{array}{c} \text{---CH}_2\text{---CH---} \\ \quad \quad \quad \\ \quad \quad \quad \text{C---OR} \\ \quad \quad \quad \\ \quad \quad \quad \text{O} \end{array}$

Membrane Preparation

Pervaporation

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 sol-

vent is evaporated overnight. Polyoctenamer and Polybutadiene membranes are cast upon Teflon plates. The next day, the elastomers are cross-linked during 45 min at 155°C. After cooling, the plates are placed in a water bath, and after 24 h, the membranes are carefully removed from the plates. The evaporation, cross-linking, and cooling step are car-

ried 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 cast on a Perspex® [poly(methyl methacrylate)] 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 .

Sorption

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 min at 155°C in a nitrogen atmosphere. After cooling, the Petri dishes are placed in a water bath, and after 24 h, the free films can be removed.

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

Sorption Experiments

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 h 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 Mulder³⁶ 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 analyzed diluted solution can be calculated. This amount should be equal to the absorbed amount of this component in the mem-

brane. Because the total mass uptake in the polymer film was also determined, the composition of the absorbed liquid in the film can be calculated according to the equations given below:

$$\phi_i = \frac{m_i / \rho_i}{\sum_{j=1}^n (m_j / \rho_j)}$$

$$n = 2(3) \text{ for binary (ternary) systems} \quad (10)$$

in which m_i [kg] is the weight of component i in the system and ρ_i [kg/m³] represents the liquid density of that component.

Pervaporation Experiments

The pervaporation experiments have been performed with a laboratory pervaporation setup, as described previously.¹⁸ A 5 L thermoregulated 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 a 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:

$$\text{Component flux: } J_i^p = \frac{m}{A \cdot t} \cdot \frac{w_i^p}{\rho_i} \quad (11)$$

in which m is the total weight of the permeate [kg]; A , the active membrane area [m²]; t , the permeation time [h]; w_i^p , the permeate weight fraction of component i [kg/kg]; and ρ_i the liquid density of component i [kg/m³]. The concentrations of the aqueous solutions of toluene and trichloroethylene, respectively, were 250 and 500 $\mu\text{g/g}$, which allows one to assume a concentration independent feed density of approximately 1000 kg/m³.

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

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

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 $10^\circ\text{C}/\text{min}$ were measured.

RESULTS AND DISCUSSION

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 to $200\ \mu\text{m}$ (see Table I) and the feed compositions chosen were about half of the maximum solubility of the components in water:

- trichloroethylene/water: $500\ \mu\text{g}/\text{g}$ (max. solubility³⁷: $1100\ \mu\text{g}/\text{g}$);
- toluene/water: $250\ \mu\text{g}/\text{g}$ (max. solubility³⁸: $500\ \mu\text{g}/\text{g}$).

The permeabilities have been calculated according to eqs. (1)–(3). The liquid boundary layer mass transfer coefficient required to solve eqs. (1) and (2) is obtained from a previous research study¹⁸ 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 toward the organic component had

been used. From a linear regression fitting procedure, boundary layer mass transfer coefficients of 2.5×10^{-5} and 2.3×10^{-5} m/s were obtained for binary aqueous solutions of toluene and trichloroethylene, respectively.

NBR Membranes

The pervaporation performance of nitrile butadiene rubber (NBR) membranes has been determined to investigate the influence of polar and slightly hydrophilic groups in the membrane material. Figure 4 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,³⁹ who studied the transport properties of gases and water vapor 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, reduction in diffusion became dominant and the water permeability dropped. As far as sorption was concerned, this explanation was endorsed by the work of Edwards,⁴⁰ 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

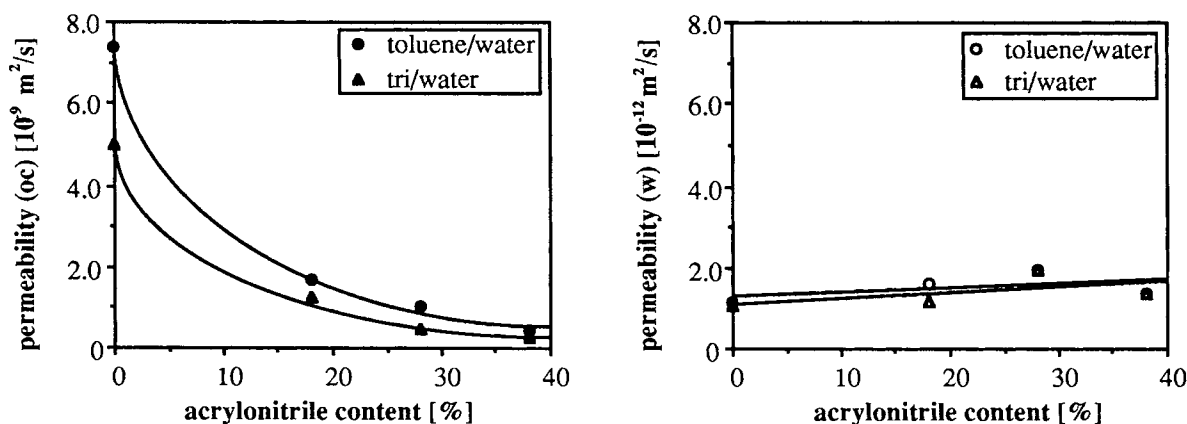


Figure 4 Permeabilities of water, toluene, and trichloroethylene in NBR membranes for the pervaporation of binary aqueous solutions.

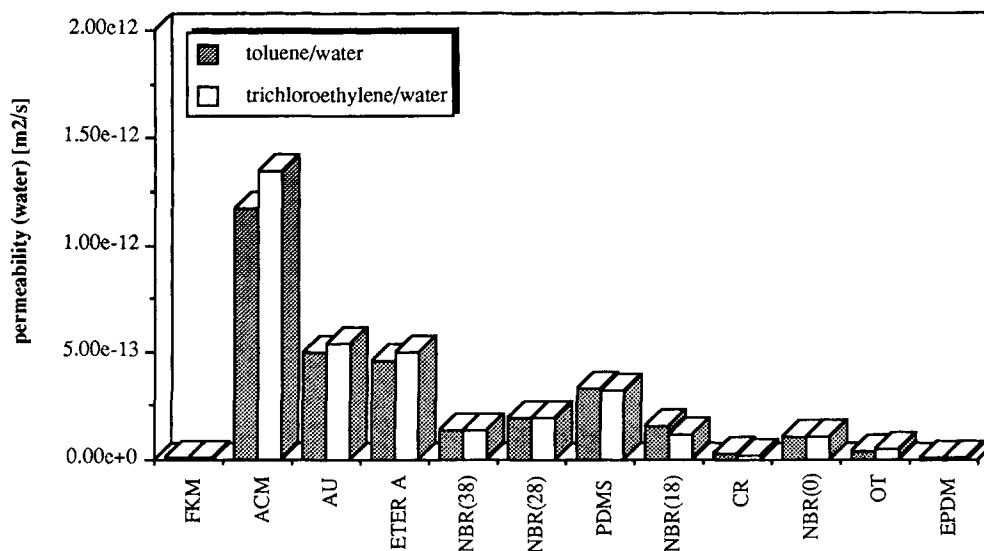


Figure 5 Intrinsic permeabilities in the pervaporation of binary aqueous solutions.

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.

NBR membranes and other copolymers of polybutadiene have also proven to be excellent model polymers in the separation of organic mixtures.⁴¹⁻⁴³ 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 nonpolar groups, e.g., in polybutadiene-based copolymers with styrene (SBR) showed that compared to NBR membranes the sorption behavior 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 behavior 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. 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 5 and 6, 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 is water. Furthermore, the water permeabilities appear to vary over a much wider range.

Interactions of water with polymers in general and with elastomers in particular have been described and reviewed extensively in the literature. Comyn⁴⁴ gave the water vapor permeabilities for several elastomers. The values for EPDM, Viton, Neoprene, nitrile rubber, and silicone rubber are 0.33, 0.40, 0.61, 4.0, and 14.0 g/m²-day, respectively. This is in reasonably good agreement with our pervaporation data, where the water permeabilities, schematically represented in Figure 5, are 0.92, 1.1, 2.5, 13, 33 × 10⁻¹⁴ m²/s, respectively.

The structural characteristics of elastomers as discussed in a previous section are often used to predict and explain permeabilities of elastomers. Iyengar⁴⁵ tried to correlate quantitatively the water vapor permeability of nonpolar 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

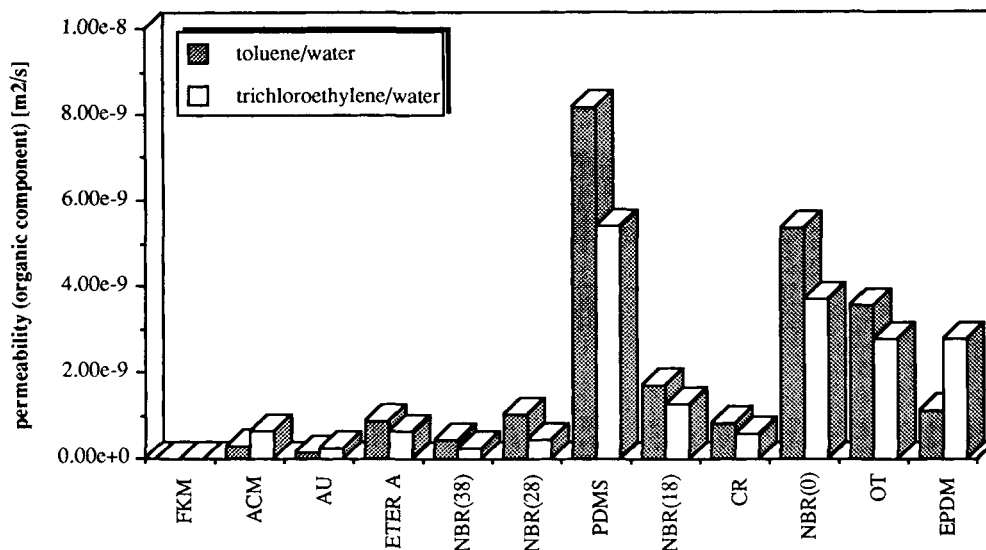


Figure 6 Intrinsic permeabilities for the organic component in the pervaporation of aqueous solutions.

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 polyoctamer (OT) are compared. These two elastomers have similar structures. 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 also be large. For membranes that exhibit a comparable sorption behavior for the organic component, the organic component fluxes will be directly related to the diffusion rates in the membrane. The molecular structures of BR and OT seem to be the most favorable ones to allow high diffusion rates, because they possess unsaturated carbon-carbon bonds and they lack any steric groups, while polar groups are absent. Figure 6 shows that good toluene and trichloroethylene permeabilities are indeed observed for these elastomers.

Again the excellent permeability of PDMS for the organic component is striking and comparable in value with those for completely nonpolar 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 behavior of the apolar membranes, for example, tend to be completely ascribed to differences in the transport rates (chain mobility), whereas sorption effects are neglected. Therefore, preferential sorption experiments have been carried out in addition. In the first attempt, the pervaporation behavior is related to structural parameters of the membrane material in a more quantitative way. The data 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 II. 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, for example, BR and OT. The effect of the rate of unsaturation is clearly shown by the latter two elastomers, which have an almost similar structure (see Table I). The only structural difference is the presence of one double bond on eight carbon

Table II Glass Transition Temperatures for the Elastomeric Membranes Studied

Elastomer	T_g (°C)
BT	-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

See Table I for explanations of abbreviations.

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.

The three-dimensional solubility parameters of the elastomers are given in Table III, both calculated from group contributions³³ and taken from the literature.^{28,30,46} In the case of polyurethane, polyacrylate 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 poly(vinylidene difluoride) and polyhexafluoropropylene is used in the calculation of the solubility parameters for the fluorinated rubbers. The calculated values are compared to data found in the 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,²⁸ whereas in the literature, deviating values have been reported for the "hydrogen-bonding parameter" of fluorinated elastomers.²⁸

Sorption

In Figure 7, the contribution of polar/hydrogen-bonding groups present in the polymer to the sorption of water is shown. The absorbed amount varies over approximately three decades. A satisfactory correlation for the sorption of water with the "combined solubility parameter" is observed. 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 8. The solubility of the organic component appears to be almost independent of the sol-

Table III Solubility Parameters of Various Elastomers and Penetrants

No.	ρ (g/cm ³)	δ_d		δ_p		δ_h		$\delta_{p,h}$		
		Calcd	Lit.	Calcd	Lit.	Calcd	Lit.	Calcd	Lit.	
Elastomer										
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	Ethylene-propylene 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		

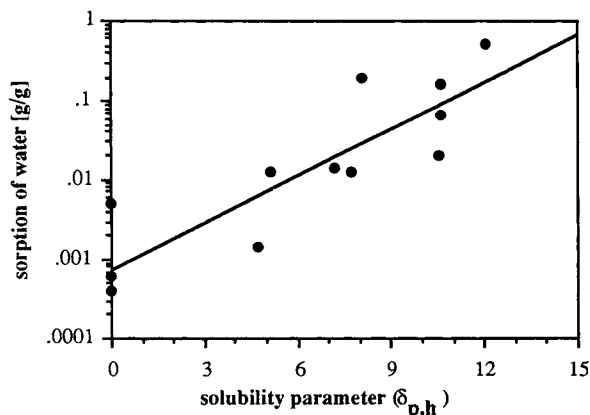


Figure 7 Water sorption for several elastomers as a function of the combined solubility parameter for polar and hydrogen-bonding contributions: $\delta_{p,h}$.

ubility parameter for polar interactions and hydrogen bonding ($\delta_{p/h}$).

From the two figures shown above, a tentative conclusion can be drawn: With respect to the sorption behavior 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.

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.

Permeabilities

In Figures 9 and 10, the permeabilities of the components of the binary liquid mixture are given as a function of the glass transition temperature. Whereas 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. 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 the data presented in Figures 9 and 10.

The water permeabilities given in Figure 10 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) has probably a dominating effect on the water flux, although the variation in the permeability data was less than three decades (as observed for the sorption data).

Summarizing, it is concluded that the highest toluene and trichloroethylene permeabilities are observed for nonpolar 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.⁴⁷

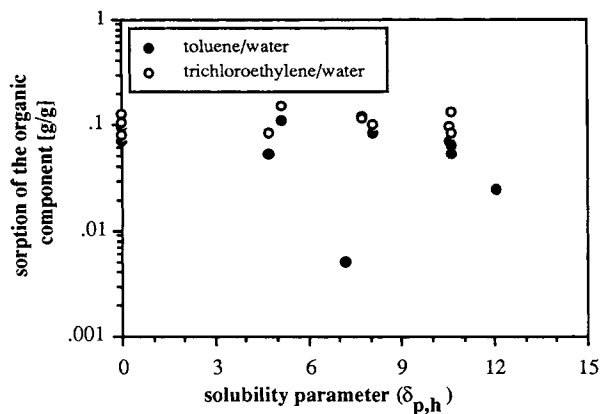


Figure 8 Sorption of the organic component for several elastomers in binary aqueous solutions as a function of the combined solubility parameter for polar and hydrogen-bonding contributions: $\delta_{p,h}$.

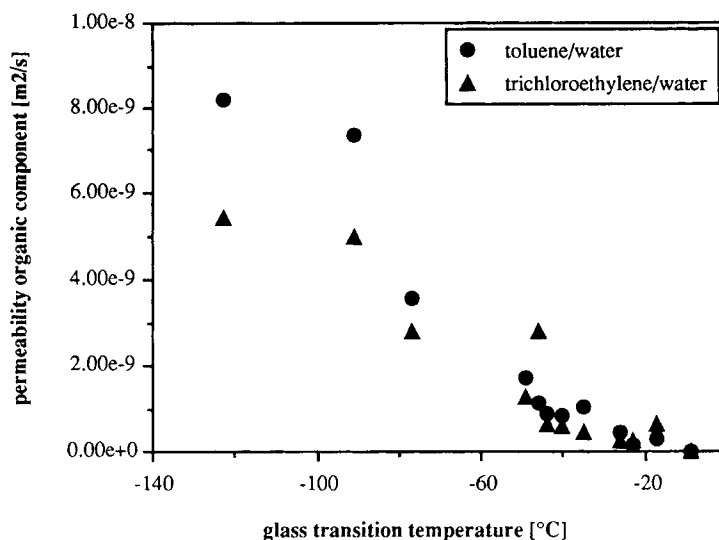


Figure 9 Dependence of the permeability for the organic component on the glass transition temperature.

Selection of Membrane Material

For the development of a thin-film composite membrane, a proper choice of the elastomeric top layer 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 $\sim 1 \mu\text{m}$ can easily be reached. A second and more important criterion 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.

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 $100 \mu\text{m}$ -thick membranes are calculated from the permeability data, values of $12 \text{ g/m}^2\text{-h}$ for PDMS membranes and $4\text{--}7 \text{ g/m}^2\text{-h}$ for the NBR membranes are obtained, whereas for ethylene-propylene terpolymer (EPDM) membranes, the water flux is about $0.3 \text{ g/m}^2\text{-h}$. As a result, the differences in se-

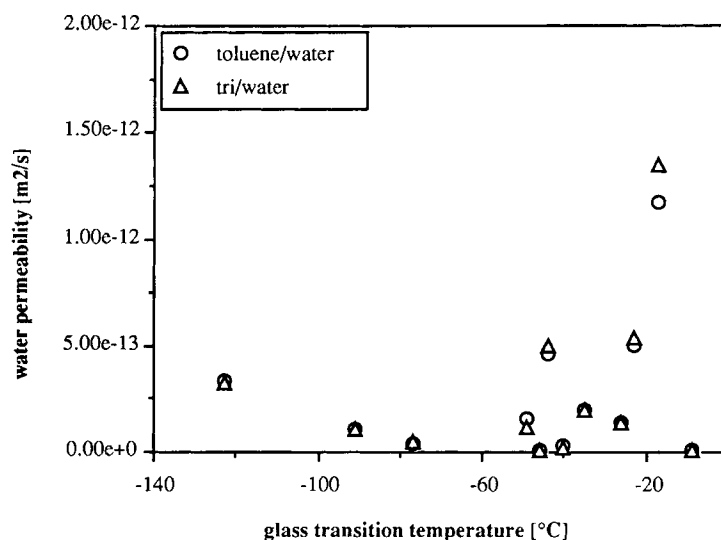


Figure 10 Dependence of the water permeability on the glass transition temperature.

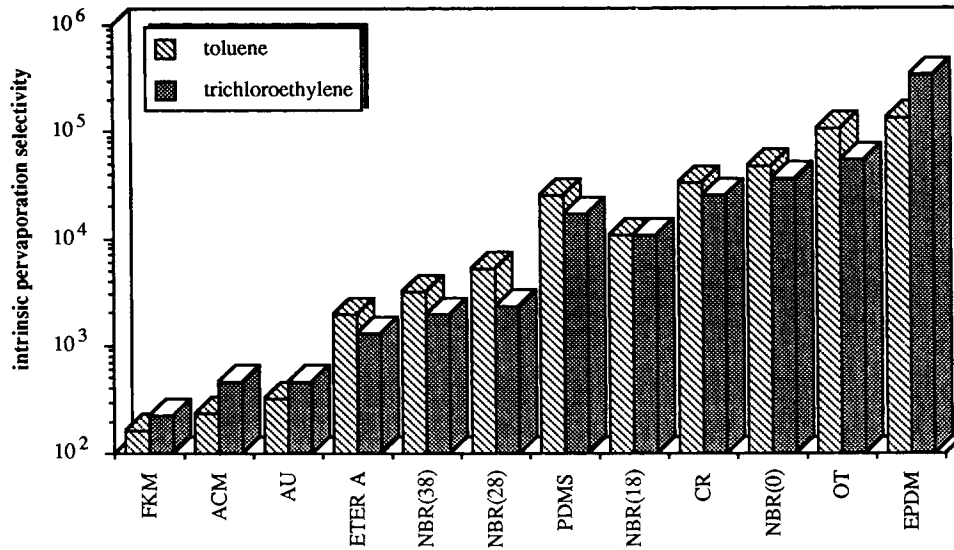


Figure 11 Intrinsic selectivities of elastomeric membranes in the pervaporation of aqueous solutions of toluene and trichloroethylene.

lectivities 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 Figs. 5 and 6).

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 eq. (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 af-

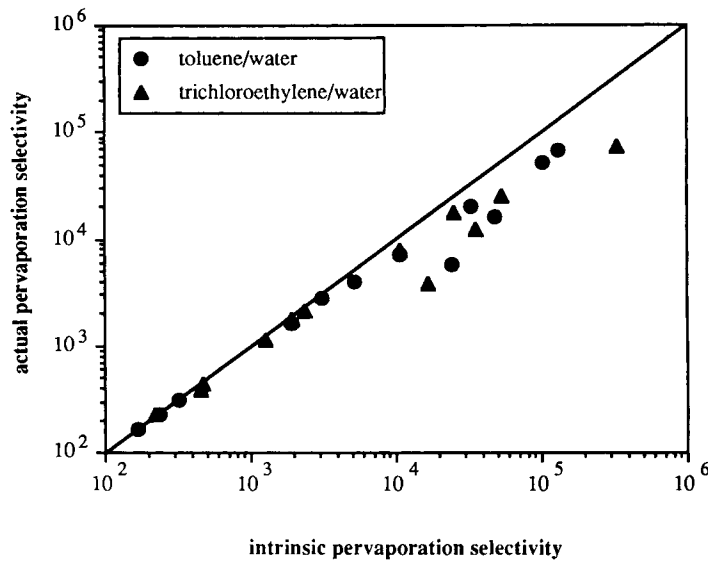


Figure 12 Observed selectivities in the pervaporation process vs. intrinsic selectivities of elastomeric membranes in the pervaporation of aqueous solutions of toluene and trichloroethylene.

ected by boundary layer effects, selectivities remain rather unaffected due to the large effect of the water permeability on the intrinsic selectivity.

CONCLUSIONS

Actual membrane permeabilities are obtained from pervaporation measurements using aqueous solutions with small concentrations of volatile organic components. To ensure the correct calculation procedure for the permeabilities, the hydrodynamic conditions are taken to be 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 (up to 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.

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