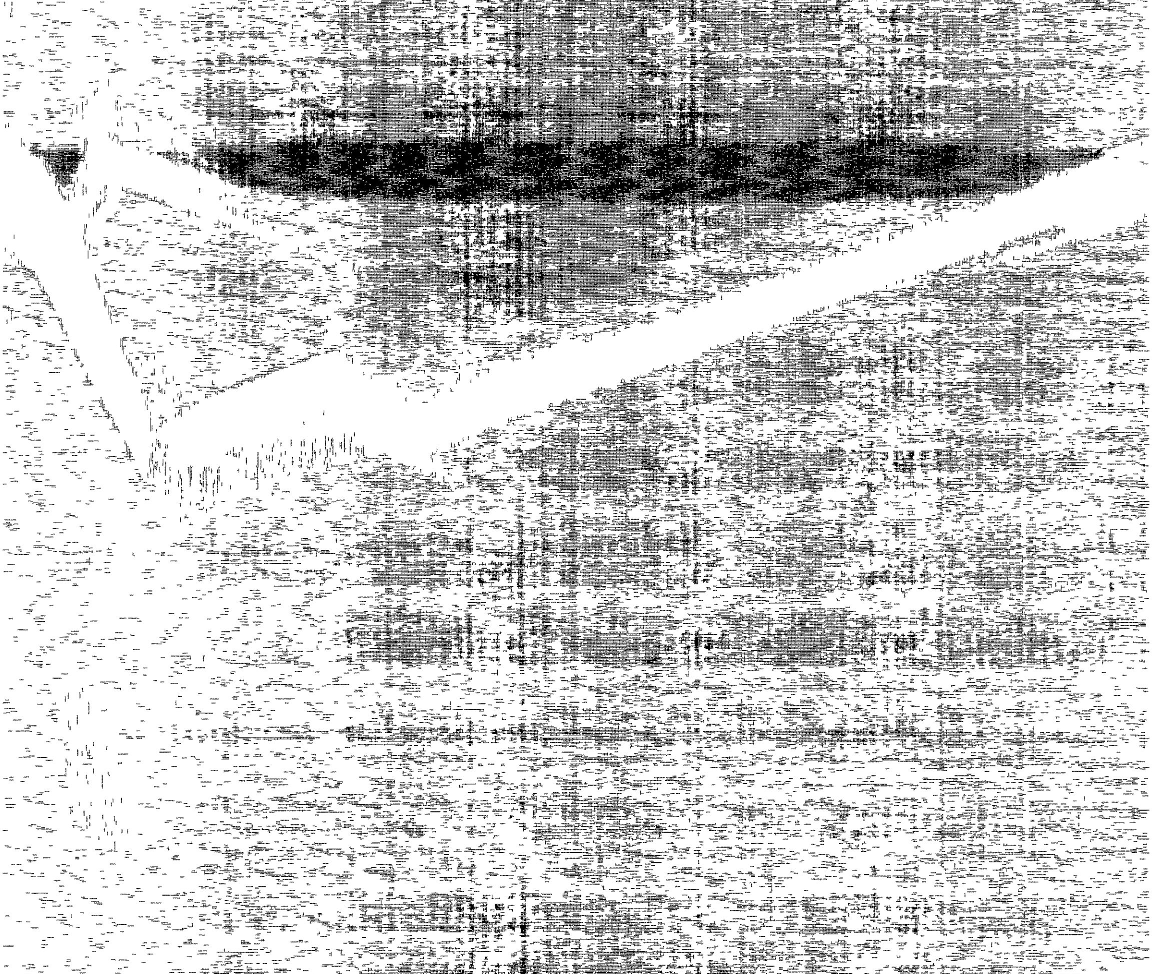
ADSORBENT FILLED POLYMERIC MEMBRANES

Application to Pervaporation and Gas Separation



Jean-Marc Duval

26

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Application to Pervaporation and Gas Separation

PROEFSCHRIFT

ter verkrijging van
de graad van doctor aan de Universiteit Twente,
op gezag van de rector magnificus,
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volgens besluit van het College van Dekanen
in het openbaar te verdedigen
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door

Jean-Marc Duval

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Preface

Il était une fois, au fin fond de Twente
Un thésard qui ma foi, n'était pas malheureux.
Étudier les membranes, c'est déjà quelque chose
Y mettre des zéolites, c'est compliquer la chose !

It is usual in a preface to acknowledge all the people involved in the final result of a Ph.D., i.e. the dissertation itself. Of course, I will follow this rule and first of all I want to thank Guy Desgrandchamps and ElF Aquitaine for offering me the opportunity to come at the Twente University, first as a "Volontaire du Service National" and then as a Ph.D. student. Kees Smolders and Marcel Mulder were my first contact in Twente a couple of months before my coming. Their guidance during my work was inspiring and fruitful. Marcel has always been ready to discuss any scientific and social problem. Besides that I appreciated him as a peculiar tennis partner who knows quite a lot about the psychological aspect of sport activities!

A Ph.D. research is not only carried out by the student himself/herself. Betty has been a very good support in carrying out the various experiments during the past three years. Furthermore she has been very patient in teaching the basics of the Dutch language to a Frenchman. I was a rather nice example of the saying: ik allochtoon, ik niet snappen! She probably remembers quite a lot of misused words and idioms leading to funny situations. Zandrie is mainly responsible for my knowledge of Dutch slang and Erik for the few words of Twents dialect I can recognize.

Also involved in my research was Antoine. His Master thesis project was difficult and somewhat frustrating, but with devotion he went on, desperately looking for a way to prepare defect free membranes. However, this did not prevent him from starting a Ph.D. in the Membrane Technology group! Among the students who carried out some of their practical training under my guidance, I want to thank Liesbeth who contributed to chapter V of this thesis by carrying out very tedious experiments in a somewhat overheated laboratory.
I am also grateful to all the other people from the university and Elf Aquitaine who participated in my project by assisting me technically or doing some chemical analyses.

Jeroen is the second "zeolite boy" in the group which means that quite a number of brainstorming sessions occurred. Many ideas and concepts in this thesis are the results of these intense discussions. I wish him good luck in investigating the many remaining ideas in this field. My thanks also to Astrid, for her support and understanding during these last three years as my room-mate, and to Matthias, whose laboratory I shared.

Last but not least the "Membraantechnologie" group as a whole was pleasant to work in because of the very nice atmosphere at the university, as well as during the many activities organized besides.

Je ne peux évidemment pas clore cette préface sans remercier les membres de ma famille et mes amis pour leur soutien durant les trois dernières années. Merci à tous.

Finalement il s'en va, avec dans sa mémoire
Des souvenirs sympas et de drôles histoires.
Ici il reviendra toujours avec plaisir
Se rappeler ce temps et aussi pour en rire !

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I

ADSORBENT FILLED POLYMERIC MEMBRANES

Introduction and state of the art

I.1- Introduction

A brief introduction on adsorbent filled polymeric membranes is not as easy as it seems to be since it brings together two fields of research which until recently were quite unrelated.

This introduction will summarize the basic principles of membrane based separations and more specifically the use of dense films for the separation of gas and liquid mixtures. Then an introduction is given on zeolites and carbon based adsorbents with respect to their structure, specific properties and current applications. The third part of this chapter is an overview of the most significant contributions in the field of adsorbent filled polymeric membranes and pure adsorbent membranes. At last, the structure of this thesis is given.

I.2- Membranes and membrane based separation processes

I.2.1- General

Many reviews on membrane based separation processes have been published in the past few years. The most recent ones are given in references [1] to [5]. Also the excellent article from Mason [6] gives an historical perspective on membrane transport. A complete description of the field is beyond the scope of this chapter and only the basic principles and points of interest for this study will be summarized to make it more clear.

A membrane may be defined as a permselective barrier between two phases [1], through which some components can pass more readily than others. The structure of the membrane is thus not taken into account in this definition.

Still quite a variety of structures can be found for practical membranes:

- symmetric:
  - homogeneous (dense).
  - porous.
  - cylindrical porous.

- asymmetric:
  - porous.
  - porous with dense toplayer (integrally skinned).
  - composite (dense skin layer of a second material brought on top of a porous sublayer).

It should already be mentioned here that in this thesis, the term composite membrane has a different definition. It stands for a membrane composed of an adsorbent phase dispersed in a polymeric phase. This is in fact the original meaning of the term composite in material science.

Another way of classifying membranes is by the separation principle. Figure 1 shows the three main principles.

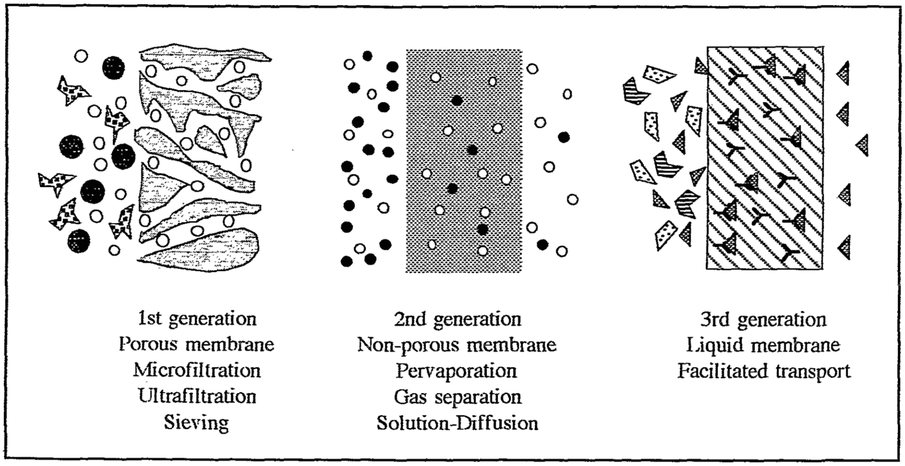


Figure 1: Structures and separation principles of three generations in membrane science.

The separation properties of the first generation, the porous membranes, are determined by the ratio of the pore sizes and the size of the particles to be separated. The membrane material itself only has an influence on fouling, cleaning, chemical and thermal stability. This type of membrane is used in micro- and ultrafiltration processes where large particles (like emulsion droplets or proteins) have to be separated from a solvent. For these membranes the separation principle is sieving.

The second generation of membranes consists of dense membranes. In this case, the separation properties are determined by differences in affinity between the species to be separated and the membrane material and also by the differences in transport rates through the membrane (solution-diffusion model). Gas separation and pervaporation are the processes based on this separation principle.

Liquid membranes are depicted as an example of a third generation of membranes. A porous support, which is usually a microfiltration membrane, contains a liquid phase in which carrier molecules are present. The liquid phase is the actual separating layer in this case. The carrier molecules are responsible for the separation, which is dependent on their binding specificity for the molecules to be separated (facilitated transport). High selectivities can be reached with this type of membrane; their stability remains a problem although improvements have been made. It must be noticed that fixed site carrier membranes do belong to the facilitated transport type of membranes but are in fact not liquid membranes.

I.2.2- Theoretical background

The processes considered in this thesis, pervaporation and gas separation, commonly make use of dense membranes. Before giving more details on these processes, the basic principles of the solution-diffusion model should be recalled as well as some definitions of relevant parameters.

The solution-diffusion model states that the transport of molecules through a dense membrane occurs in three steps:

- sorption of the penetrating species into the membrane material;
- diffusion of the dissolved species through the membrane;
- desorption at the permeate side.

The overall transport properties are controlled by the selective sorption into and diffusion of molecules through the membrane material.

The separation properties of a certain material are given by its permeability coefficient (P) and selectivity (α):

Permeability (P) = Solubility (S) x Diffusivity (D)

For an ideal mixture the selectivity α is defined as:

$$\alpha_{A/B} = P_A / P_B$$

where P_A and P_B are the permeabilities of the components A and B for a binary mixture.

The solubility, a thermodynamic parameter, is the amount of penetrant sorbed by the membrane material at equilibrium.

The diffusivity is the proportionality constant between the flux of a component through a plane perpendicular to the direction of diffusion and the concentration gradient as expressed by Fick's first law:

$$J = -\mathbb{D}\frac{dc}{dx}$$

The flux is mostly given in terms of partial pressure difference:

$$J_i = \left(\frac{P_i}{l}\right)\Delta p_i$$

with P_i : permeability coefficient for component i ($mol.m.m^{-2}.s^{-1}.bar^{-1}$)
l : membrane thickness (m)
Δp_i : partial pressure difference across the membrane (bar)

Furthermore, one may consider the permeation of species through a polymer film as an activated process and thus define an activation energy of permeation E_p so that:

$$P(T) = P_o \exp(-E_p/RT)$$

From a simple Arrhénius plot where ln(P) is plotted versus 1/T, the activation energy of permeation can be obtained from the slope.

I.2.3- Pervaporation

Pervaporation is a quite recently developed separation technique. The separation mechanism follows the solution-diffusion model, i.e. the separation is achieved by means of differences in solubility and diffusivity in the membrane material. The feed mixture is in the liquid state and the permeate is a vapor. This means that at least the energy of vaporization of the transported species must be supplied to the system. The driving force for transport is a difference in activity or a partial pressure difference over the membrane. This driving force is commonly applied by means of a vacuum or a sweep gas at the permeate side, which ensures a low activity. The permeate is usually recovered by condensation. On laboratory scale, the feed mixture is typically at room temperature and the permeate is collected by a cold trap (liquid nitrogen). On industrial scale, the feed is often at high temperatures (slightly below the boiling point) to increase the permeate flow and to generate a driving force. The permeate is collected by condensation with cooling water.
Nowadays, quite a number of plants for the dehydration of organic solvents are running (e.g. dehydration of ethanol) and material studies are carried out to apply pervaporation to the dehydration of more aggressive solvents (for instance acetic acid [7]). Another application on pilot plant scale is the removal of trace organics from water [8-10]. Much of the research effort is focussed on the development of new membrane materials which could be used for the

separation of other mixtures, like polar/non-polar organics [11-13].

1.2.4- Gas separation

Gas separation is usually achieved by cryogenic distillation or absorption processes. However two new techniques are emerging: Pressure Swing Adsorption and membrane separation. Pressure Swing Adsorption is discussed in a following section.

Separation of gaseous mixtures by means of membranes can be achieved by using four different types of membranes.
The first industrial gas separation membranes were porous, with pores in the range of 50 to 100 Å, thus smaller than the mean free path of a gas molecule at ambient pressures. This separation mechanism is known as Knudsen diffusion. In this case the separation factor is inversely proportional to the square root ratio of the molecular weights of the two gas species. This means that for small differences in molecular weight, no significant separation factor is to be expected.

Molecular sieve membranes are nowadays more and more investigated in order to separate gas mixtures. They consist of a porous structure with pores smaller than 7 Å in diameter. This type of membrane is further described in the literature review (section 4 of this chapter).

Liquid and fixed site carrier membranes also show very interesting gas separation properties for certain gaseous mixtures (see review paper by Way and Noble [14]). The application of specific carriers results in high selectivities for the oxygen/nitrogen separation. However, the stability of the carrier and the membrane itself remain serious drawbacks, as well as the upscaling to industrial applications of such membranes (decrease of membrane thickness). This explains why this type of membrane has not reached beyond the laboratory scale yet.

The membranes used at the moment are mostly of the solution-diffusion type. Polymer materials with a very broad range of separation properties can be found (see figure 2). However, one can see that in the case of the CO_2/CH_4 separation high permeabilities are usually coupled with low selectivities and vice versa. This is a general trend which is valid for any gas mixture.
Nowadays most of the research aims at developing high performance polymers like polyimides [15] , polyoxadiazoles or polytriazoles [16], i.e polymers having both a high selectivity and a relatively high permeability. Another incentive is the improvement of the membrane structure in order to maintain the intrinsic selectivity of the material with a very high productivity by decreasing the effective thickness of the separating layer [17].

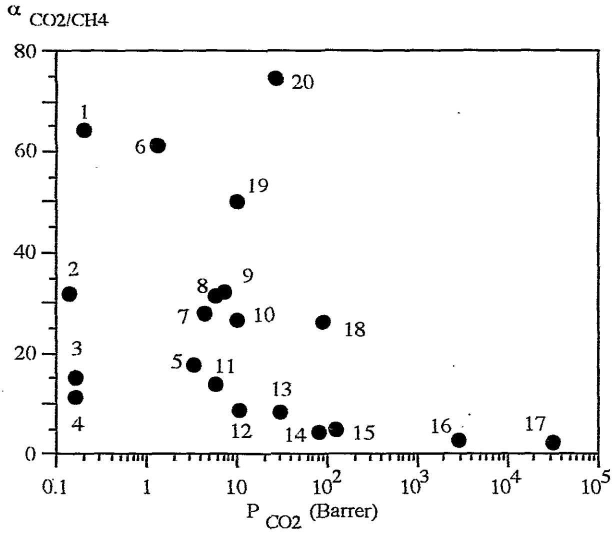


Figure 2: Selectivity for carbon dioxide over methane versus carbon dioxide permeability for various polymers; 1-PI (Kapton), 2-PET (Mylar),3-PVC, 4-Nylon 6, 5-NBR50, 6-PEI, 7-PSF, 8-CA, 9-PES, 10-PC (Lexan), 11-NBR45, 12-PS, 13-PCP, 14-EPDM, 15-Natural rubber, 16-PDMS, 17-PTMSP, 18-PIDA-POD, 19-PT 75/25, 20-PI 6FDA-4,4'ODA (see appendix 3 for chemical structures); data experimentally determined or from references [1,15,16].

The main applications of membranes in gas separation are summarized in table 1.

However, until now, the membrane based gas separation process is not very widely utilized, because it has to compete with the already well established techniques like absorption for natural gas sweetening or cryogenic distillation for air separation and other emerging processes like Pressure Swing Adsorption (PSA). In an excellent overview, Spillman compared the economics of membrane based separation processes to conventional techniques for hydrogen recovery, natural gas sweetening and air separation among the possible applications [18]. He demonstrated that membranes are highly competitive for relatively small scale applications where not extremely high purities are required. The lack of confidence in new processes in general and the response of non-membrane competitors, however, make the real market entry of membranes long and difficult.

Application	Gas mixture	Product(s)
Hydrogen recovery from ammonia purge gas	H_2 / N_2	H_2
Hydrogen ratio adjustment in synthesis gas	H_2 / CO	H_2
Hydrogen recovery from hydrogenation processes	H_2 / hydrocarbons	H_2
Natural gas sweetening Sour gas treatment Enhanced oil recovery	CO_2 / H_2S / hydrocarbons	CH_4
Natural gas dehydration	H_2O / hydrocarbons	hydrocarbons
Oxygen enriched air	O_2 / N_2	O_2
Nitrogen enriched air	O_2 / N_2	N_2
Air drying	H_2O / air	dry air
Vapor recovery	volatile organics / air	clean air + organics recovered
Helium recovery	He / N_2	He

Table 1: Applications of membranes in the field of gas separation (adapted from [16] and [18]).

I.3- Adsorbents

I.3.1- Carbon based adsorbents

Active carbons

Active carbons can be manufactured from any kind of raw material provided it has a high carbon content and a low inorganics content. The main raw materials are wood, coal [19], lignite, coconut shell, peat and also polymeric materials.
The manufacturing process is conducted in two steps. First carbonization of the raw material at about 800°C in an inert atmosphere which results in the decomposition of non carbon species. Here the rate of heating and the final temperature are the main parameters for the quality and yield of the carbonized product. The second step is the activation which is aimed to obtain a porous structure. It can be carried out either physically (carbonization in an oxidizing atmosphere) or chemically (impregnation with an activation agent followed by a heat treatment in an inert atmosphere).
In both methods temperature, atmosphere and duration of the activation process are the main parameters determining the obtained properties.
The microporous surface area of active carbons prepared in this way is typically

in the range of 1000 to 2000 m^2/g. The pore size distribution is wide as can be seen in figure 3.

Obviously, the adsorption of a molecule is influenced by the size of the pores. Despite this, in the case of conventional active carbons, the pores are too large to enable any significant size exclusion effect of simple molecules.

Active carbons are generally considered as hydrophobic materials. Nevertheless, the surface properties of the carbonaceous adsorbent play a major role in the adsorption process [20-23].
Active carbons are always associated with appreciable amounts of oxygen. The oxygen is fixed firmly and the only way to remove it is a high temperature treatment in an inert atmosphere or in vacuum (outgassing). Hence the competitive adsorption of polar molecules is greatly influenced by the presence of surface oxygen groups, like CO- or CO_2- complexes [20]. A reversal of the sorption selectivity in a liquid mixture methanol/benzene is observed when the carbon is outgassed. However, in most cases active carbons show a selective sorption for the aromatic compounds in a mixture with alcohols, especially in the low concentration range for the aromatic component. The selectivity is higher if the carbonaceous adsorbent is totally outgassed.

The main fields of application for active carbons are in medical care (poisoning treatment), water treatment [24-27], air purification [28], decolorization processes and also as support for catalysts.

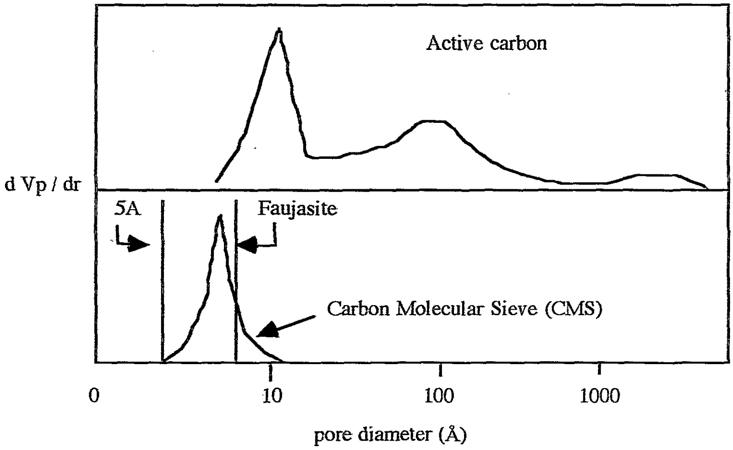


Figure 3: Schematic pore size distributions of the adsorbents considered.

Carbon Molecular Sieves

A new class of carbon based adsorbents are Carbon Molecular Sieves (CMS). They are produced by thermal decomposition in a controlled chemical and thermal environment of a non melting polymer material or by carbonization of coal [29-32].
The main difference between CMS and active carbons is, that the pore size distribution is much narrower and the mean pore size is in the range of molecular dimension (5-7 Å) for the former type (see figure 3). The control of the pore size can be carried out by a mild oxidation in air (400°C), carbon dioxide or steam. Coal can also be treated with hydrocarbons under cracking conditions in order to deposit carbon exactly at the pores mouth, thus resulting in a decrease of the pore openings without a large decrease of the microporous volume [33,34].

The main applications of CMS are in the separation of molecules by molecular sieving. For instance in gas separation, the Pressure Swing Adsorption process makes use of a difference in adsorption rate to separate oxygen/nitrogen [35-37], carbon dioxide/methane [35,36,38] and other gaseous mixtures [39,40]. However, this process cannot be run continuously with one adsorption bed; it requires the use of at least two adsorbent beds which are alternatively in the sorption and the desorption mode (figure 4).

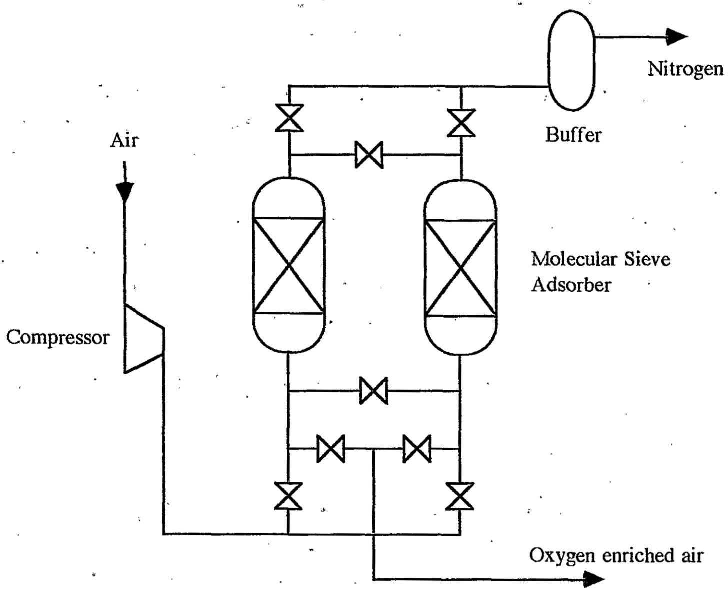


Figure 4: Schematics of a Pressure Swing Adsorption installation applied to air separation (adapted from [15]).

I.3.2- Zeolites

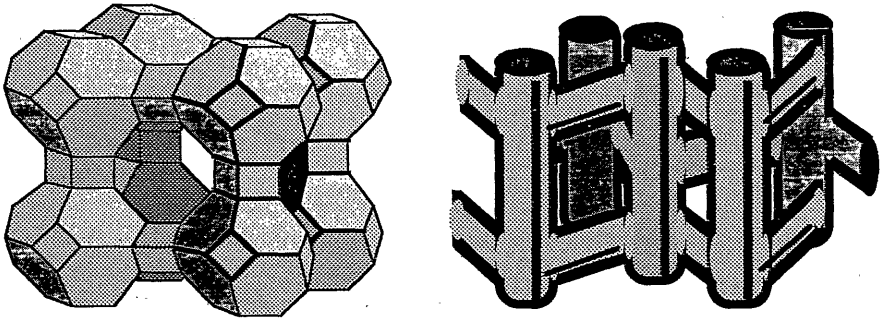
General

According to Breck, one of the pioneers in the field, zeolites are crystalline, hydrated aluminosilicates (as formed in nature or synthesized) with cations of group I and group II, in particular Na, K, Mg, Ca, Sr and Ba [41,42]. Zeolites can be represented by the empirical formula $M_{2/n}O.Al_2O_3.xSiO_2.yH_2O$. In this formula n is the cation valence, x is greater than or equal to two and y is a function of the porosity of the framework, the Si/Al ratio and the cations present. The water molecules, together with the cations, reside in the interconnected pores and channels present in the structure.

Structural investigations showed that zeolites are crystalline, microporous, inorganic polymers. The framework consists of a three dimensional network of SiO_4 and AlO_4 tetrahedra, linked to each other by sharing the oxygen atoms. The size of the zeolite pore opening is determined by the number of tetrahedra required to form the pore and the nature of the cations present in or at the pore entrance. These cations are present to balance the negative charge introduced into the framework by the substitution of Si^{4+} by Al^{3+}. Because of the presence of the cations, aluminum-rich zeolites all show a high affinity for water coupled with a fairly high saturation capacity (≈ 25 wt%).
Zeolites are thermally stable materials, i.e. they can stand temperatures up to 700°C for the least stable species. The stability is roughly inversely related to the amount of aluminum in the framework [42].

Few fields of chemistry offer such chemical and structural diversity as the area of zeolites. Although only 85 different structures are known [43], from which only eleven are used commercially, tens of thousands of theoretical structures are possible (but not synthesized yet). Figure 5 shows the structures of zeolites LTA (Linde Type A) and MFI (ZSM-5, silicalite-1), two of the most industrially used zeolites. For a more complete overview of zeolite structures, one should consult reference [43] and the appendix to chapter IV of this thesis where a detailed description of the zeolites used in the present study is given.

Zeolite LTA is a very hydrophilic zeolite as a result of the high aluminum content (Si/Al=1) which causes the presence of a large number of hydrated cations. The channel structure is built of large cavities connected by smaller apertures, the so-called eight membered oxygen rings. This results in a three dimensional pore structure, consisting of three intersecting channels running through the structure [44]. The cation in the type A zeolites can be either Ca^{2+}, Na^+ or K^+, resulting in the so-called 5A, 4A and 3A zeolites, respectively.



LTA (type A)
Si/Al = 1
3.2, 3.8, 4.3 Å
3D

Pentasil, MFI (ZSM-5, silicalite-1)
$10 < Si/Al < \infty$
5.2*5.7 Å <-> 5.3*5.6 Å
2D

Figure 5: Schematics of the porous structure of zeolites LTA and MFI.

The structure of zeolite Faujasite looks a bit like the structure of type A zeolites, except that in the cubic array of the building units one out of eight units is missing. This results in a larger pore opening: 7.4 Å instead of 3 to 4.3 Å for the type A zeolites. The difference between X and Y zeolites is the result of differences in the Si/Al ratio, which is somewhat higher for the type Y zeolite.

The zeolites mentioned above are all hydrophilic. A major breakthrough took place in 1972, when a patent was filed for the synthesis of the first high silica zeolite by Mobil, ZSM-5. Almost at the same time, the pure silica analog, with the same framework structure, was prepared by Union Carbide and named silicalite-1. The pore structure of this zeolite (Pentasil or MFI) is shown in figure 5. A ring of ten oxygen atoms controls the access to the silicalite channels, and this is the reason why these zeolites are intermediate in their molecular sieving behaviour between the eight ring zeolite A and the twelve ring zeolites X and Y. Silicalite-1 and ZSM-5 have two sets of intersecting channels, one straight and the other sinusoidal and therefore a so called two dimensional pore structure results. Silicalite-1 exhibits organophilic properties due to its very high Si/Al ratio.

One must know that ZSM-5 and silicalite-1 are not the only high silica containing zeolites. High silica Y zeolites (ultrastable Y denominated as USY) can be prepared by dealumination, resulting in Si/Al ratios up to 100-200. Another example is zeolite Theta-1 (TON).
Furthermore, new extra large pore zeolites have recently been prepared, like cloverite (13.2 x 4.0 Å) [45] and the MCM-41 family (16 to 100 Å depending on the surfactant used during the synthesis) [46].
At last, a new generation of adsorbents is now emerging, like the aluminophosphates (AlPO's), the silicoaluminophosphates (SAPO's) and their metal doped analogues (MAPO's and MAPSO's) where the metal (M) can be Li, Be, Mg, Cr, Mn, Co or Zn [42,47]. These adsorbents offer new properties with regard to pore

size, hydrophilic properties and catalytic properties, though their stability in the presence of water remains a major problem, as well as their availability. These new generation molecular sieves have not been considered as filling materials in the present study.

Synthesis

Certain zeolites can be found in nature. However, in order to obtain an adsorbent or a catalyst whose properties are reproducible and controllable, synthesis methods have been worked out in the past 40 years to prepare these products industrially. The three types mentioned previously (LTA, Faujasite, Pentasil) constitute about 90% of the market if the non-regenerative applications of the naturally occurring zeolites such as clinoptilolite are excluded. The scope of this chapter is not to describe the synthesis procedures in detail. The reader should consult references [41], [42], [44] and [48] to obtain more knowledge about this intensively investigated topic. Nevertheless, one might say as a rule of thumb that the synthesis method of the most common zeolites is based on the hydrothermal crystallization of reactive alkali metal aluminosilicate gels at low temperatures and pressures. The mechanism is generally assumed to involve solution mediated crystallization of the amorphous gel and cation templating in some cases (MFI for instance). The template cation shows structure ordering, i.e. water ordering properties. These water molecules around the cation might be partially replaced by silicate and aluminate anionic tetrahedra. In this way the template cation acts as a crystal building unit.

Sorption and molecular sieving effect

As a result of the very sharp pore size distribution which is present in zeolites, they show a rather sharp cut-off with increasing molecular size. Therefore zeolites can act like almost perfect filters for molecules, due to size and/or shape differences between the zeolite aperture and the adsorbate. This effect is called molecular sieving. In order to correlate the pore size of a zeolite with the dimensions of various adsorbate molecules, a scale of molecular dimensions should be established. In the early experiments, the molecular size was based upon the equilibrium diameter of the adsorbate molecule, calculated by using the known molecular shape, bond distances, bond angles and van der Waals radii. This approach was not very satisfactory, since it was observed that certain molecules were freely adsorbed despite the fact that in the non-adsorbed state they were larger than the known aperture of the zeolite crystal. Therefore, mostly the collision or kinetic diameter is used [41].

For spherical and non-polar molecules, the potential energy of interaction $\phi(r)$ is well described by the Lennard-Jones (6-12) potential:

$$\phi(r) = 4\,\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

in which σ and ε are characteristic constants of the molecular species. They can be obtained from measurements of second virial coefficients, gas viscosity and molecular beam scattering experiments [49].

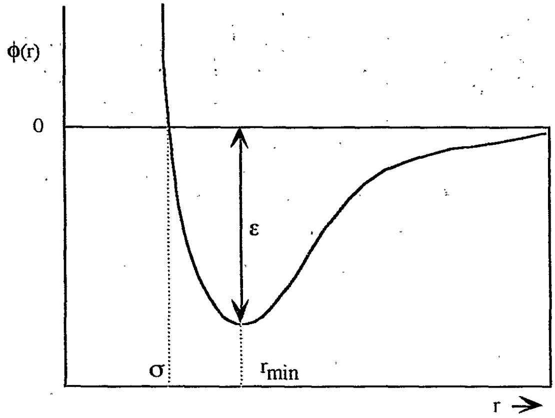


Figure 6: Potential energy of interaction versus distance of approach (adapted from [41]).

In figure 6 one can notice that the maximum energy of attraction, ε, occurs at r_{min}, with r_{min} equal to $2^{1/6}\sigma$ [41]. When the potential $\phi(r)$ equals zero, the diameter r is the same as σ. The kinetic or collision diameter is the intermolecular distance of closest approach for two molecules colliding with zero initial kinetic energy. For non-polar spherical molecules, the constant σ is equal to the kinetic diameter, and σ values obtained from minimum cross-sectional diameters are used for more complex molecules. Figure 7 shows the correspondence between the pore sizes of various zeolites and the kinetic diameters of a few molecules.

Here it must be clearly said that the separation properties of zeolites are not only a result of size exclusion effects, but also the adsorption interactions in zeolites play an important role. The forces causing the adsorption can be divided into van der Waals forces and electrostatic forces. On a non-polar surface such as activated carbon and high silica zeolites, only the van der Waals forces are significant. Therefore, molecules are adsorbed with an affinity approximately proportional to the molecular weight (neglecting size exclusion effects). Most zeolites, however, have a number of (exchangeable) cations and are therefore polar adsorbents. As a result molecules like ammonia (high dipole), CO_2 or N_2 (quadrupole) and aromatic hydrocarbons (π layer interaction) are preferentially adsorbed over non-polar species of comparable molecular weight

[50].

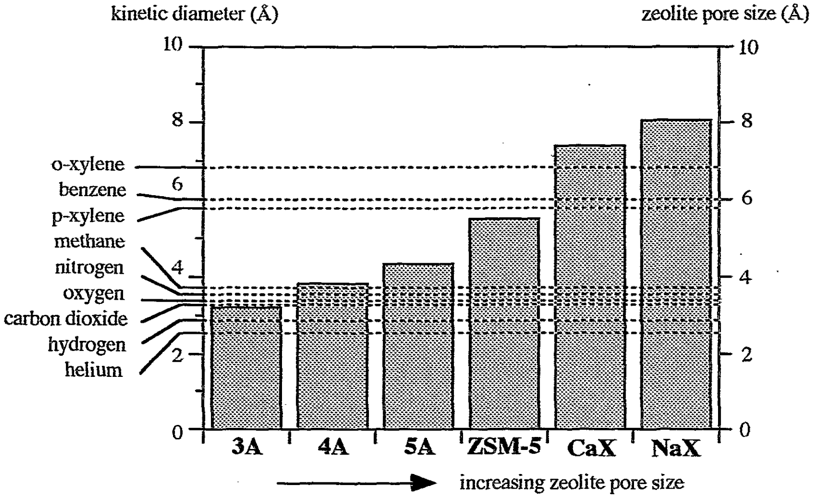


Figure 7: Correspondence between kinetic diameter and zeolite pore size (adapted from [50]).

Also of importance are the valence and size of the cations which are present in the zeolite. The affinity of zeolites for polar or quadrupolar molecules generally increases with increasing cation charge and decreasing cation radius (although this effect is strongly masked by the presence of water of hydration). Furthermore, the shape of a pore and its size may also have an effect on sorption behaviour of certain zeolites. The van der Waals energy of a molecule sorbed in a pore of atomic size, will be maximal when its dimensions match intimately with that of the surrounding pore. Such a molecule may then acquire supermobility (the so-called floating molecule [51]). In other situations, a serpetine or creeping motion of chain molecules along the channel walls may be expected. It has indeed been shown that this effect takes place and that sometimes diffusion coefficients for floating molecules are reported which are three orders of magnitude larger than for creeping molecules [52]. Because the research area of the sorption of gases and liquids into zeolites is very large, one is referred to the literature for more specific data.

Applications

Some of the naturally occurring zeolites (clinoptilolite, chabazite, mordenite) find some industrial applications in soil amendement, odor control, animal feed and pollution control [53]. In all these applications, the zeolite is not regenerated.

The main application of synthetic zeolites is in the detergent industry where environmental considerations have led to the gradual withdrawal of phosphates from detergents (this application represents roughly 85% of the zeolite market which was about 1 million tons in 1991 [53]). In this case zeolite A (4A) is used because of its high ion exchange capacity which allows the fast removal of calcium ions (and magnesium to a smaller extent) from the wash water [54].

The second application of synthetic zeolites in order of importance is in the field of catalysis in the petrochemical industry (about 10% of the market [53]). The catalytically active sites are confined within the microporous zeolite pore system which means that the hydrocarbon molecules react in a shape-selective manner. The most significant applications are cracking catalysts (zeolite USY or rare earth Y constitute 97% of the zeolite catalysts), hydrocracking catalysts (USY), dewaxing (ZSM-5, mordenite), paraffin isomerization (mordenite based), ethyl benzene production (ZSM-5, USY), xylene isomerization (ZSM-5) and methanol-to-gasoline process (ZSM-5) [55,56].

At last adsorptive separation processes make use of zeolites because of their unique specific sorption properties [50,57]. In this case the zeolites are, most of the time, in the form of pellets which are formed by using a binder. The first type of applications are the purification processes. Drying of gases and solvents is achieved using hydrophilic zeolites like 3A or 4A [50,53] and the removal of CO_2 and H_2S traces is possible with zeolites 4A and 5A. In this case the regeneration is carried out by a thermal cycle. The bulk separations constitute the second class of adsorptive applications. The separation of linear paraffins in the gas phase uses zeolite 5A with various techniques (PSA, chromatographic). Zeolites 5A and 13X are used to separate air by Pressure Swing Adsorption using the equilibrium sorption selectivity for nitrogen of these hydrophilic zeolites (the product is thus oxygen). On the other hand zeolite 4A can be used for the kinetic separation of air by Pressure Swing Adsorption (the product is nitrogen in this case).

New applications of zeolites are likely to appear in the next few years. For more details one should consult reference [58].

I.4-Literature review: Use of adsorbent materials in membrane applications

As mentioned previously, adsorbent materials are conventionally applied in a semi-continuous way, i.e. by using adsorption/desorption-regeneration cycles. However, investigations in order to use their specific separation properties in a continuous manner have been carried out for about 25 years, more or less successful. During the past ten years, the most significant studies were published, which clearly showed the possibility of using carbon based materials or zeolites to improve the separation performance of polymer materials or as a pure separative phase.

I.4.1 - Carbon based materials

Usually people have been trying to use a pure carbon phase to manufacture a membrane. As far as we know, only one paper reports on the incorporation of a carbon molecular sieve into a polymer phase and its use as a membrane material [59]. In this investigation, an epoxy-diacrylate prepolymer containing 30 wt% of active carbon was photochemically grafted onto cellulose. The resulting gas separation properties show that the transport mechanism may occur by a strongly activated process and by Knudsen diffusion. Despite this, high separation factors for carbon dioxide over methane are reported.

The first publications on purely carbon membranes described the preparation of porous membranes by compaction of carbon powder [60-63]. These membranes exhibit a high internal surface area. Separation is achieved by adsorption of one of the components. This adsorbed dense film prevents the transport of the other components through the pores. No molecular sieving effect is observed in this case. Hence high separation factors were observed for mixtures like SO_2/H_2 and CO_2/N_2. This can be compared to publications on porous ceramic membranes for the gas phase separation of water/ethanol mixtures [64]. In this case water condenses in pores smaller than 3 nm thus hindering ethanol transport. The resulting separation factors were up to 8 for water.

Bird and Trimm [65] were among the first who really investigated the use of carbon molecular sieves as a membrane material. However, the transport of gases through their membranes occurred both in large interstices and on the surface of the micropores.

Koresh and Soffer [66,67] developed a carbon molecular sieve hollow fiber membrane. This membrane is manufactured by controlled pyrolysis of a carbon containing precursor (cellulose, cellulose derivatives, thermosetting polymers) resulting in pores in the molecular dimension range. In addition, these membranes show good chemical and thermal stability. However, the mechanical stability remains a major drawback. Interesting O_2/N_2 separation properties were reported for these membranes. The transport mechanism is assumed to be governed by the presence of constrictions in the micropores which results in a fast and selective diffusion of the gas molecules.

Another preparation technique is dip-coating of a carbon porous support by a polymer solution [68] or a latex suspension [69]. After drying and controlled pyrolysis, the pore size of the support is greatly reduced, and consequently the gas permeability as well. However the transport mechanism is still a combination of viscous flow, Knudsen flow and activated diffusion, which means that the measured selectivities are low.

I.4.2 - Zeolites

Zeolite/polymer composites

The first reported studies on the incorporation of zeolitic adsorbents into polymers are about 20 years old.

In 1973, Paul and Kemp [70,71] investigated the influence of zeolite 5A on the gas permeation (N_2, CO_2, CH_4) and sorption properties of a silicone rubber material. They showed that the presence of the zeolite results in an increase of the permeation time-lag, a slight decrease of the steady-state gas permeability and a large increase of the sorption capacity. The aim of this research was to develop a protective coating, and thus not to improve the separation properties of the polymer phase. However their conclusion on the application of zeolites to improve the barrier properties of polymer materials is not correct. The phenomenon observed with zeolite 5A cannot be generalized to other zeolitic adsorbents, as is shown in this thesis.

In 1971, Rhône-Poulenc filed a patent on the use of zeolite containing polymer films in a semi-continuous way (adsorption-reactivation/desorption) [72].
In 1976 Wolf et al. published on the incorporation of zeolites 4A and 5A into a copolymer ethylene-vinyl acetate used in gas separation [73]. It was found that the separation of a mixture of four components (CH_4 / C_2H_4 / C_3H_6 / C_4H_8) changed from butene/propene selective for the pure polymer to methane selective for the 5A filled polymer.

More recently, Sterzel and Sanner filed a patent on a polymer phase containing a zeolite which is claimed as being effective in the separation of carbon dioxide from hydrocarbons [74].

Kulprathipanja et al. described the use of filled membranes in two membrane processes in two patents [75,76]. First a cellulose acetate membrane filled with silicalite-1 showed an improved O_2/N_2 selectivity (2.99 for the pure polymer and a maximum of 4.06 for the filled polymer) and also an improved CO_2/H_2 selectivity (0.70 for the pure polymer and 9.6 for the filled polymer). However, no permeability data were given. Secondly some cellulose acetate membranes were used to separate monosaccharides from higher saccharides in aqueous solution. The fillers considered are the zeolites CaY and silicalite-1 as well as active carbons. The addition of the filler resulted in an increase of the flux with a constant retention, which was independent of the filler type. Furthermore, the author suggests ways to improve the adhesion between the zeolite external surface and the glassy polymer, without indicating whether the final structure of the membranes tested was defect free or not, i.e. whether voids were present around the zeolite particles.

One of the most significant contributions in the field came from te Hennepe et al. in a study on silicone rubber membranes doped with zeolites and applied to the pervaporation of alcohols/water mixtures [77-79]. Their results showed that the organophilic zeolite silicalite-1 does enhance the selectivity for ethanol and also the flux of the composite membrane (figure 8).

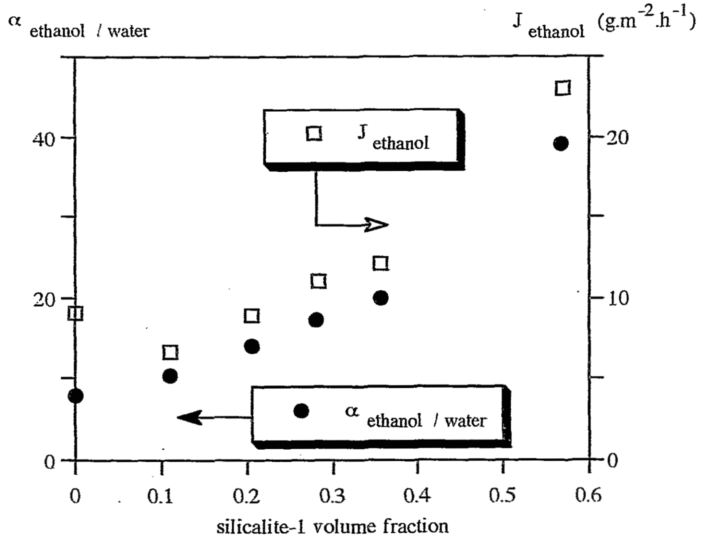


Figure 8: Ethanol/water selectivity and ethanol flux versus the volume fraction of silicalite-1 in a silicone rubber membrane (adapted from [79]); the flux is normalized to a membrane thickness of 100 μm, the feed consists of 5 wt% ethanol in water and the temperature is 25°C.

This breakthrough was explained by an increase of the ethanol concentration in the membrane due to the presence of the organophilic zeolite and to a fast sorption-desorption step in the zeolite which allows the zeolite to take part in the transport. The same trend was observed with methanol and propanol. These results turn out to be in contradiction to the publications of Paul and Kemp [70,71]. However, it should be emphasized that for such systems, the zeolite considered as well as the permeating species are determining the effect observed upon incorporation of the zeolite into a polymer phase. This explains why two opposing conclusions can be drawn from these two studies with respect to the effect of zeolites on the permeation properties of polymeric materials.
It seems that the study of te Hennepe et al. gave a second start to the field when considering the number of publications which have appeared since 1988 and are related to this work.

Jia et al [80,81] reported pervaporation and gas separation results with the same type of membrane. They proved that silicalite-1 improves the O_2/N_2 ideal selectivity of silicone rubber from 2.15 to 2.92 and they defined a facilitation factor which, when plotted against the kinetic diameter of the gas molecules, gave a clear indication of a molecular sieving mechanism in the zeolite pores (figure 9).

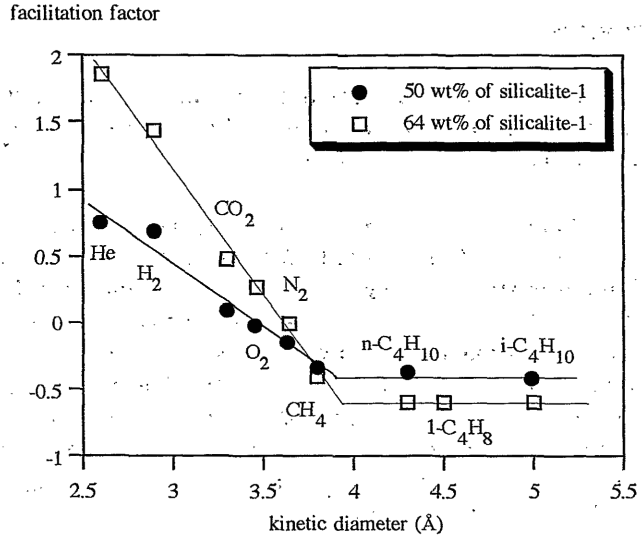


Figure 9: Facilitation ratio ($(P_{z+p} - P_p)/P_p$) versus kinetic diameter (adapted from [80]) in the case of silicalite-1 filled silicone rubber membranes; P_{z+p} is the permeability of the filled polymer and P_p is the permeability of the pure polymer.

In figure 9 it can be seen that the smaller the molecule, the higher the facilitation ratio. When the considered molecules are too large, they simply do not diffuse through the zeolite pores, as indicated by the horizontal line.
In a more recent communication [81], the preparation of a thin-film (3 μm) of silicalite-1/silicone rubber composite was reported, focussed on the pervaporation of ethanol/water again. The remarkable result of te Hennepe et al. was confirmed, i.e. an increase of both ethanol selectivity and flux by the incorporation of the zeolite into the silicone rubber matrix.

Goldman et al. [82] investigated the influence of zeolite NaA (4A) on a modified PVC membrane with respect to its ethanol/water pervaporation properties. They showed that the water selectivity could be increased from 7 to 29 and the water permeability from 7.10^{-5} to 4.10^{-4} $g.m^{-1}.h^{-1}$. The enhanced transport of water was explained by the existence of an interfacial phase between the zeolite and the polymer, which would be much more permeable to water.
The most recent publication concerning zeolite filled polymeric membranes again reports on the pervaporation of alcohol/water mixtures by means of ZSM-5 filled silicone rubber membranes [83]. The influence of the Si/Al ratio of the zeolite has been investigated, showing a decrease in alcohol selectivity when the Si/Al ratio decreases, i.e. the zeolite becomes more hydrophilic.
Finally Demertzis et al. [84] investigated the potential of zeolites embedded in a low-viscosity epoxide resin as ion-exchange membrane. The performance of the membranes were mainly determined by the degree of adhesion between

the polymer phase and the zeolite (see appendix 2 to this thesis).

Zeolite membranes

In order to characterize the permeation properties of the zeolite itself, the most elegant way is to prepare a membrane where the zeolite phase is directly in contact with the feed and the permeate.

The first investigations tried to embed a single crystal of zeolite in a gas tight phase. Wernick et al. [85] studied the permeation of isobutane and methane/isobutane mixtures through a single NaX crystal. Very long time-lags were observed, indicating the important role of the hydrated cation present in the zeolite in the establishment of steady state permeation.
Hayhurts and Paravar [86] reported on the permeation of C_1 to C_5 n-paraffins through a single crystal of silicalite-1 embedded in an epoxy resin. The diffusion coefficient of the various gases were determined by a time-lag method. The results show that there is a linear relationship between the logarithm of the diffusion coefficient and the logarithm of the number of carbons in the gas molecule. It is also suggested that the diffusion coefficients determined represent only the resistance to mass transfer due to configurational interactions (narrow channels of the zeolite) because silicalite-1 is free of aluminum and cations which means that the adsorptive interactions are very weak. Geus et al. [87] published a similar study (single silicalite crystals in epoxy resin) indicating that the selectivity is governed both by sorption and diffusion. Other techniques to prepare zeolite membranes from large zeolite crystals have been published (sol-gel, Chemical Vapor Deposition [88], dip coating [89]).

Bein et al. [90] prepared a zeolite-silica composite from suspensions of small zeolite crystals in a tetraethylorthosilicate solution which is hydrolyzed and polymerized. The suspension is dip-coated and while the solvent evaporates, the incorporated zeolite freezes in. These films can be prepared with various zeolites and utilized to introduce chemical selectivity to highly sensitive surface acoustic wave devices.

Nowadays, the incentive is to prepare directly a zeolite film on a support. Several studies have been published in the last five years.
Suzuki [91] filed a patent on the preparation of an ultrathin zeolite membrane (A, X, Y, ZSM-5) on a porous support (metal, polymer, Vycor glass). Sano et al. [92] prepared non-supported ZSM-5 films in the range of 2 to 3 cm^2. The films turned out not to be homogeneous, i.e. they are more crystalline at the outer side than at the inner. Furthermore no attempt of separation of any mixture was reported, probably due to the poor mechanical stability of these films. More recently they presented results on the synthesis of the same type of films using cellulose moulding as support [93], but no application as membrane material was suggested.

Haag et al. also reported on the synthesis of a ZSM-5 film [94,95]. This film does not contain any macropores, but the various measured selectivities indicate the probable occurrence of a binary transport mechanism (molecular sieving and Knudsen flow).
Geus et al. [96] presented recently some permeation results obtained with an in situ grown ceramic MFI type film. Low selectivities were obtained for binary mixtures (Ne/isobutane), where the permeation rate is governed by the slowest moving species (isobutane). This happens in the case of high partial pressures of isobutane in the feed. However, within the Henry sorption range, higher selectivities for neon were obtained, which is due to a lower adsorption of isobutane in the pores, hence making them available for neon diffusion. A similar type of membrane was prepared by Jia et al [97], but here again the transport of the molecules cannot be totally ascribed to activated diffusion in the zeolite pores.

I.4.3 - Conclusions

This literature review shows that zeolites are able to improve the separation properties of polymer materials, provided the correct zeolite and polymer are chosen. On the other hand, active carbons have not been extensively investigated as filler in a polymer phase, but more as a pure separative phase (carbon membranes) showing interesting properties, even if the mechanical stability remains inconvenient.
The last development in the field, besides zeolite-polymer composites, is the large number of studies aiming at synthesizing and using pure zeolite membranes. These membranes would have the advantage of being chemically and thermally stable, and also mechanically when prepared on an appropriate support. Until now, the available results do not prove that the transport of molecules only occurs through the zeolite pores. However, the published studies are encouraging and a breakthrough may be expected in the next few years.
The last conclusion is that until now, no extensive study has really been carried out in the field of adsorbent filled polymeric membranes. The investigations were only based on one or a few zeolites or carbonaceous adsorbents in one polymer and for a given application. This thesis does certainly not pretend to cover the whole range of adsorbents and polymers available and all types of applications, but by carefully selecting significant adsorbents, polymers and applications, the authors wish to elucidate what are the determining factors of improvement and to get a better understanding of the transport mechanism. Furthermore, adsorbent filled polymeric membranes may be considered as a fourth generation of membranes, giving a combination of characteristics as incorporated by the three generations mentioned in a previous section. Hence, the polymer phase is dense but the zeolites and carbons are microporous materials. In addition adsorbent particles can be seen as fixed site carriers in the polymer phase. This means that the present study deals with a hybrid type of membrane which can be considered under various specific aspects.

I.5- Structure of this thesis

This dissertation investigates the effect of incorporation of microporous adsorbents on the separation properties of dense polymeric membranes in pervaporation and gas separation.

Chapter I gives a short introduction on polymeric membranes, adsorbents and composite membranes.

In chapter II, the effect of carbonaceous adsorbents on the separation properties of polymer materials has been studied in the case of the pervaporation of a toluene/ethanol mixture. Zeolites are considered here only to a minor extent.

Chapter III demonstrates the effect of a few selected zeolites on the gas separation properties of rubbery polymers for a mixture of carbon dioxide and methane and for oxygen/nitrogen separation. Carbon molecular sieves are also investigated and the results are given in the appendix to this chapter.

The properties of the zeolites and their influence on the gas separation properties of filled polymeric membranes are studied in chapter IV. Pore size and pore directions, chemical composition and the extent of activation are the parameters which have been investigated.

Chapter V aims at understanding the transport mechanism through zeolite filled polymeric membranes better by studying the effect of process parameters (temperature, pressure, time effect) on the permeation properties. Significant differences are observed depending on the type of zeolite considered.

Finally, chapter VI discusses the possibilities of modelling the experimental results in various ways and the significance of the modelling with respect to the zeolite transport properties.

At last various methods to incorporate zeolite particles into glassy polymer materials are described in an appendix.

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II

SEPARATION OF A TOLUENE/ETHANOL MIXTURE BY PERVAPORATION USING ACTIVE CARBON FILLED POLYMERIC MEMBRANES

Summary

In order to improve the separation properties of dense polymeric membranes towards a toluene/ethanol mixture, various active carbons and two types of zeolites were introduced into a thin polymeric film in order to form a heterogeneous membrane composed of solid particles surrounded by a polymer phase. Active carbons show a high adsorption selectivity for an aromatic compound over ethanol in the low concentration range of the aromatic component. Sorption and pervaporation experiments were carried out with a toluene/ethanol mixture showing no improvement in selectivity and a decrease in flux for membranes filled with active carbons. For zeolite filled membranes both selectivity and flux decreased. A permeability model derived for heterogeneous systems was used which confirmed that the carbon particles have a closed porous stucture allowing no transport from one side to the other and that the zeolites have an ethanol selective permeation behaviour.

II.1- Introduction

In order to influence the separation performance, the incorporation of carbonaceous materials into a polymeric membrane has been investigated. Active carbons are widely used in adsorption processes because of their high adsorption selectivities towards certain compounds (chlorinated hydrocarbons in water for example [1-2]). In addition, the molecular sieving properties can be applied in the field of gas separation (oxygen/nitrogen and carbon dioxide/methane separation by Pressure Swing Adsorption [3-4]). This work was undertaken to enhance the flux and selectivity of a dense polymeric membrane by incorporation of active carbons, based on the selective properties of these materials to increase preferential sorption. From literature it is known that the addition of silicalite-1 in silicone rubber membranes results in an increase of both flux and selectivity for alcohol in the separation of alcohol/water by pervaporation [5].

Active carbons show a high preferential adsorption selectivity for aromatic compounds in solution with alcohols, especially in the low concentration range of the aromatic compound [6-9]. This behaviour was experimentally observed from adsorption experiments in the liquid phase. Hence, the separation of a mixture of toluene and ethanol by pervaporation was investigated, using active carbons with various porous structures and two zeolitic adsorbents as microporous fillers. Finally, the pervaporation results are interpreted in terms of a permeability model which was derived for heterogeneous sytems [10,11].

II.2- Materials

II.2.1- Active carbons and zeolites

A complete and detailed description of the specific characteristics of active carbons is beyond the scope of this study. In summary, active carbons are porous carbonaceous materials manufactured from various raw materials (coal, wood, polymers). Their internal porous volume and pore size are strongly dependent on the raw material used and the manufacturing process, i.e. the activation conditions. For instance, the internal surface area can reach values up to 1500 m^2/g and a porous volume of 2 cm^3/g. Pores are found in the range of molecular dimensions (sub-micropores, diameter<1 nm) as well as in the macroporous range (diameter>100 nm). For more details, the reader should consult references [12] and [13] and chapter I of this dissertation.

The active carbons used in this study were kindly supplied by CECA S.A. (France) and NORIT N.V. (The Netherlands). Table 1 gives the characteristics of the different active carbon samples used, according to the data given by the two manufacturers.

active carbon	V_{tot} ($cm^3.g^{-1}$)	V_{micro} ($cm^3.g^{-1}$)	bulk density ($g.cm^{-3}$)
CP	2.10	0.25	0.27
4S	0.97	-	0.31
L4S	0.97	-	0.31
GAC 1240	0.95	0.35	0.48
Cecalite	0.52	0.18	0.63
SX Ultra	1.40	0.39	0.29
SA2	0.95	0.31	0.41
W20	0.55	0.22	0.60

Table 1: Active carbon characteristics (data from manufacturers).

The active carbons available have quite different porous volumes, going from a rather macroporous stucture (CP, SX Ultra) to a molecular sieving one (CECALITE, W20). Furthermore, a carbon black, Printex 60 (Degussa, Germany) was used as a non-porous reference filler with a particle size of 21 nm and a BET surface area of 115 m^2/g. This, for example, can be compared to a value of 1300 m^2/g for the active carbon 4S.

Besides active carbons, two different zeolites were used. Zeolites are crystalline alumino-silicates whose internal structure forms a network of microvoids and pores. Pore size is typically in the molecular sieving range (<1 nm) (see [14-16]). The first zeolite investigated was NaY with a Si/Al ratio of 20. This high ratio makes this zeolite less hydrophilic than the normal zeolite NaY (Si/Al=2.7); thus the former presumably is toluene selective with respect to sorption. The pore size of this zeolite is 7.4 Å. Furthermore silicalite-1 (UOP, USA), the pure siliceous form of zeolite ZSM-5 was also investigated because of its organophilic properties [17]. This zeolite has a pore size of about 5.5 Å.

II.2.2- Polymers

Active carbons are sorption selective for the aromatic compound in a mixture with an alcohol, and consequently polymers have to be chosen with a selectivity for the aromatic compound as well. Hydrophobic polymers meet this requirement. Ethylene-propene rubber (Keltan 578, DSM) was used as a first choice. Furthermore, an ethylene-vinyl acetate copolymer (Elvax 150 (33% vinyl acetate), DuPont), silicone rubber (polydimethylsiloxane (PDMS), prepared from RTV 615 A and RTV 615 B, General Electric) and a series of Nitrile Butadiene Rubbers with various amounts of acrylonitrile (NBR, Krynac 2750, 3450 and 4550, Polysar) were investigated (27, 34 and 45 represents the content of acrylonitrile based on NBR). Table 2 gives an overview of these different polymers.

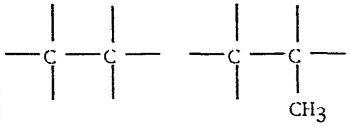
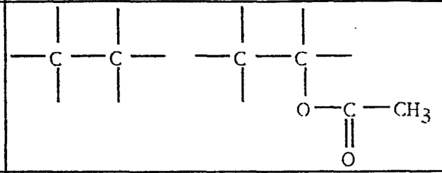
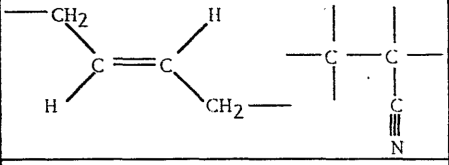
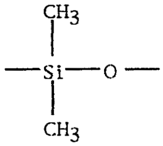
polymer	molecular structure	density ($g.cm^{-3}$)
Ethene-propene rubber (EPDM) Keltan 578		0.86
Poly-(ethylene-vinyl acetate) 33% vinyl acetate (EVA) Elvax 150		0.95
Nitrile Butadiene Rubber (NBR) 27, 34, 45% acrylonitrile Krynac 2750, 3450, 4550		0.98
Polydimethylsiloxane (PDMS) RTV 615		1.02

Table 2: Overview of the polymers investigated.

II.3- Experimental

II.3.1- Adsorbent preparation

Active carbons

The active carbons used had to be grinded before incorporation into the polymeric matrix because particles up to 150 μm were present into the samples provided. Grinding was achieved by stirring the carbon particles with glass balls in ethanol during several weeks. This mild process resulted in particle sizes below 10 μm as was observed by Scanning Electron Microscopy. The active carbons were then activated at 150°C for 24 hours under vacuum and then stored under vacuum at room temperature.

Zeolites

Prior to use, the zeolite NaY was activated at 350°C for 2 hours and then kept in a vacuum oven. In the case of silicalite-1, the activation was carried out at 500°C in order to calcine the organic template employed during the synthesis.

II.3.2- Membrane preparation

Ethylene-propene rubber (EPDM), nitrile-butadiene rubber (NBR) and poly(ethylene-vinyl acetate) (EVA) membranes

The adsorbent was first stirred in the solvent (n-hexane for EPDM, chloroform for EVA and NBR) during two hours in order to break the clusters of particles. The polymer was then added and stirring was carried out until a homogeneous dispersion was obtained. Dicumylperoxide (Merck) was used as cross-linking agent in the case of EPDM (6 weight%) and EVA (4 weight%). Dibenzoylperoxide (Merck) was used in the case of NBR (10 weight%). The solution was stirred for two more hours and then cast on a Teflon™ plate after air bubbles had been removed. Evaporation was carried out overnight under a nitrogen stream and followed by a cross-linking reaction at 155°C for 1 hour in a nitrogen atmosphere for dicumylperoxide curing and at 110°C during 45 minutes for dibenzoylperoxide. The resulting membranes were about 100 μm thick.
The solvents (analytical grade) for dissolving the polymers and the cross-linking agents were used without further purification.

Polydimethylsiloxane (PDMS) membranes

The two components of RTV 615 (prepolymer and curing agent in a ratio 9:1) were mixed with the active carbon until a homogeneous dispersion was obtained. After removal of air bubbles, the paste obtained this way was cast on a Teflon™ plate. The cross-linking reaction was carried out at 80°C for 16 hours. The resulting membranes were about 100 µm thick.

II.3.3- Adsorption experiments

The characterization of porous adsorbents with respect to their sorption selectivity in the liquid phase has not yet been very well described. Often a species which does not sorb is used as a reference to calculate sorption selectivities (with zeolites as adsorbent for example). However, in the case of active carbons, the broad pore size distribution makes the selection of a non-adsorbable component impossible. Nevertheless, it is possible to compare different adsorbents by a depletion method.

In this method a standard amount of adsorbent ($m=1g$) is incorporated into a standard amount of a liquid mixture ($m_0=10g$) with a certain composition which is determined by gas chromatography. After sorption equilibration (24 hours at 30°C was applied), the liquid phase is analysed again and the change in its composition is then determined which gives the depletion in weight fraction of one of the components, Δx. Then the surface excess $m_0\Delta x/m$ can be calculated, which allows to compare different adsorbents with respect to their adsorption selectivity for a component, e.g. for toluene. The same method can be used with a polymer and a filled polymer. These experiments were carried out with 10 weight% of toluene in ethanol and also with 10 weight% of ethanol in toluene.

II.3.4- Pervaporation experiments

A detailed description of the experimental set-up is given in appendix 1 to this thesis.

The pervaporation experiments were carried out with a mixture of toluene and ethanol (10 and 90 weight% respectively). The temperature of the feed mixture was kept at 30°C and the downstream pressure below 0.1 mbar. Steady state conditions were reached after three hours. Then the first sample of permeate was collected in the liquid nitrogen cold trap and analysed by gas chromatography. This was repeated over a period of two to four days in order to control the variation in time.

II.4- Results

II.4.1- Adsorption by depletion

Table 3 and figure 1 summarize the results obtained from the depletion method with active carbons, zeolites and pure polymers. In this table a positive sign means preferential adsorption of the minor component in the liquid mixture.

adsorbent	surface excess toluene 10/ethanol 90	surface excess toluene 90/ethanol 10
CP	20	-
4S	14	-
L4S	13.5	-
GAC 1240	12.7	-
Cecalite	10.4	-
SX Ultra	14	-
SA2	12.1	-
Printex 60	0.8	-
silicalite-1	0.4	-
NaY Si/Al=2.7	- 1.6	25.6
NaY Si/Al=10	- 0.3	-
NaY Si/Al=20	0.2	19.7
EPDM	6	-
PDMS	5.1	-
EVA	5.2	-

Table 3: Adsorption experiments by the depletion method; a positive sign indicates preferential sorption of the minor component in the liquid mixture; T=30°C.

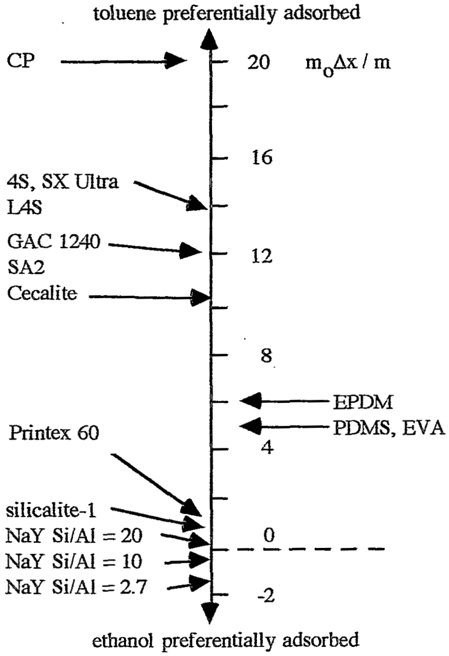


Figure 1: Adsorption experiments by the depletion method; surface excess obtained with 10 g of feed (10 wt% toluene in ethanol) and 1 g of adsorbent or polymer.

In a mixture consisting of 10 weight percent toluene in ethanol the carbons show a much larger surface excess than the organophilic zeolite silicalite-1

(figure 1). This is the result of the larger porous volume of the carbons. Furthermore the effect of aluminum content in the zeolite framework can be seen in the case of zeolite NaY. For example NaY with a Si/Al ratio of 2.7 is ethanol selective, whereas NaY with a ratio Si/Al of 20 is slightly selective for toluene.
This could be expected because the aluminum atoms in the framework bear a negative charge which is balanced by a counter ion, thus making the surface more hydrophilic depending on the amount of aluminum. Hence decreasing the amount of aluminum results in a less hydrophilic zeolite. The carbon black (Printex 60) does not show a very large surface excess for toluene due to its non-porous structure, i.e. adsorption can only take place on its external surface.

The polymers used in this study were also tested. The surface excess values obtained are much lower than of the active carbons which means that the polymers considered are less sorption selective than the active carbons (the experiments were performed with the same amounts of sorbent and liquid feed, respectively) or sorb less.
On the other hand, the hydrophobic zeolites do not seem to be selective enough to improve the separation properties of the polymers.

From table 3, it can be seen that with a mixture of 10 weight% ethanol in toluene, the more hydrophilic zeolites NaY resulted in a large surface excess for ethanol, which means that in this concentration range they are selective for ethanol. Here again a larger amount of aluminum results in a more ethanol selective behaviour.

II.4.2- Pervaporation

The selectivity for a liquid mixture is defined as

$$\alpha_{\text{toluene / ethanol}} = \frac{\left(\frac{x_{\text{toluene}}}{y_{\text{ethanol}}}\right)_{\text{permeate}}}{\left(\frac{x_{\text{toluene}}}{y_{\text{ethanol}}}\right)_{\text{feed}}}$$

and the flux values have been normalized to a membrane thickness of 100 µm.

Unfilled polymers

Table 4 shows the pervaporation results obtained with the various polymers investigated.

membrane	$\alpha_{\text{toluene / ethanol}}$	$J_{100\mu m}$ ($g.m^{-2}.h^{-1}$)
NBR 45	3.4	70
NBR 34	4.6	145
NBR 27	5.6	194
EVA	8.9	300
PDMS	13	800
EPDM	62	60

Table 4: Pervaporation properties of various rubbery polymers; feed: toluene/ethanol (10/90 wt%); T=30°C.

One can see from this table that PDMS and EVA are high flux polymer materials with a rather low selectivity for toluene.

The series of NBR shows a decreasing organic flux and toluene selectivity when the acrylonitrile content increases. The larger the amount of acrylonitrile, the better the chemical resistance of the polymer and the lower the overall sorption, and consequently, a decrease of the total organic flux can be observed. On the other hand, acrylonitrile segments make the polymer matrix more hydrophilic and rigid than polybutadiene, which means that the larger the amount, the more ethanol sorption and diffusion selective the matrix which can explain the decrease in toluene selectivity.

At last, EPDM is the most selective polymer investigated but shows the lowest total flux.

Active carbon filled membranes

Figures 2 and 3 show the variation of the selectivity and flux for various active carbons incorporated into an EPDM matrix.

All these results show that the selectivity of the membrane remains mainly constant when an active carbon is incorporated into the polymeric matrix for all carbons tested. On the other hand, the total flux through the membrane is decreased drastically by the addition of these carbon particles.

Furthermore, one can see from table 5 that polymers with different separation performances for the studied mixtures (large flux and low selectivity or low flux and high selectivity) show the same behaviour upon addition of active carbon particles. The porous structure of the latter has no effect at all, i.e. active carbons with large pores or a carbon molecular sieve (table 1) do not show any difference with respect to the pervaporation performance.

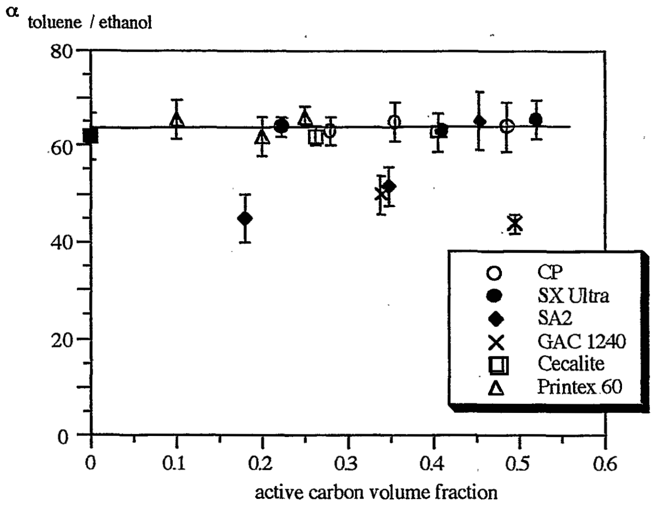


Figure 2: Pervaporation selectivity of active carbon filled EPDM membranes versus the volume fraction of active carbon in the membrane; feed: toluene/ethanol (10/90 wt%); T=30°C.

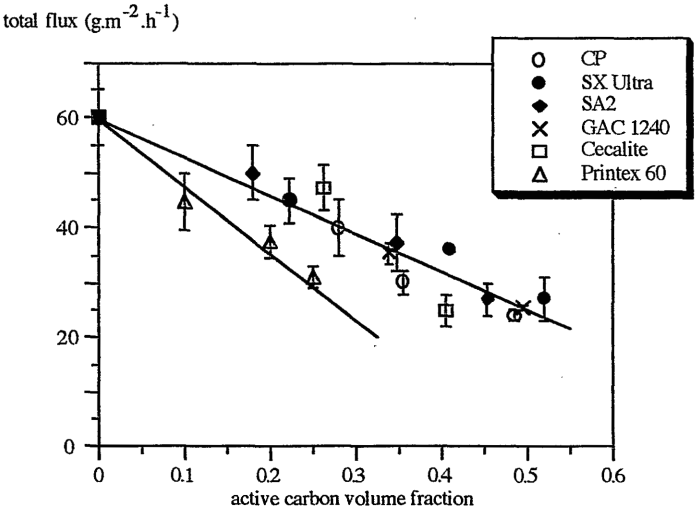


Figure 3: Total pervaporation flux (normalized to a membrane thickness of 100 μm) through active carbon filled EPDM membranes versus the volume fraction of active carbon in the membrane; feed: toluene/ethanol (10/90 wt%); T=30°C.

membrane	$\alpha_{toluene/ethanol}$	$J_{100\mu m}$ (g.m^{-2}.h^{-1})
EPDM	62	60
EPDM + CP 48.6 vol%	64	21
EPDM + SX Ultra 52 vol%	65	27
EPDM + W20 28 vol%	70	27
EPDM + NaY20 31 vol%	26	36
EVA	8.9	300
EVA + CP 45 vol%	7.9	225
EVA + 4S 24 vol%	9.4	180
NBR 45	3.4	70
NBR 45 + SX Ultra 44 vol%	3.7	43
NBR 45 + SX Ultra 55 vol%	3.4	37
PDMS	13	800
PDMS + W20 31 vol%	14	570

Table 5: Effect of active carbons on the pervaporation properties of various polymers; feed: toluene/ethanol (10/90 wt%); T=30°C.

The results obtained with the carbon black Printex 60 are also plotted in figures 2 and 3. This non-porous carbonaceous material shows the same behavior as porous active carbons with respect to the pervaporation selectivity and a somewhat larger decrease of the total flux at equal volume fraction of particles in the membrane. This last phenomenon could be due to the very small particle size (20 nm) of carbon black, which results in a much larger contact surface area between the polymer and the carbon phase than with particles in the micrometer range. This may affect to some extent the physical cross-linking of the polymer matrix, as was described by te Hennepe [11] and Briscoe et al. [18].

Zeolite filled membranes

In table 5 and figure 4, the pervaporation data obtained for the polymer EPDM, pure and with zeolites NaY (Si/Al=20) and silicalite-1 are given. One can observe that the trend is the same as with active carbons with respect to the flux through the membrane and in addition a decrease of the selectivity was measured by incorporation of these zeolites into the polymer matrix. These results will be discussed in a following section.

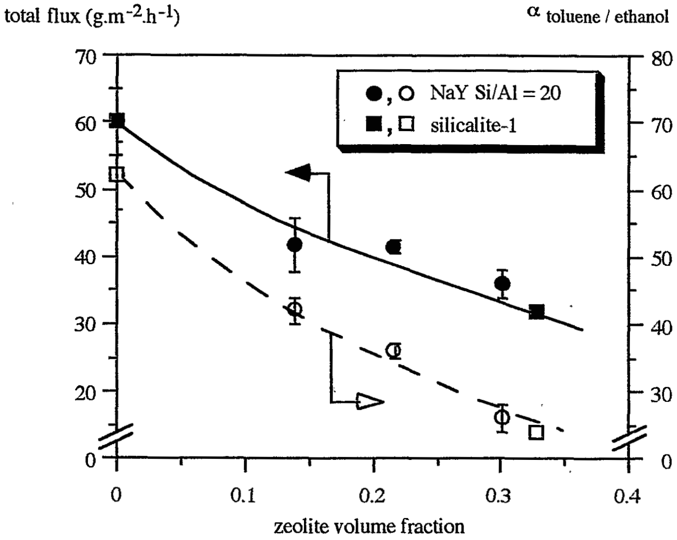


Figure 4: Toluene/ethanol pervaporation selectivity and total pervaporation flux (normalized to a membrane thickness of 100 μm) of zeolite filled EPDM membrane versus the volume fraction of zeolite in the membrane; feed: toluene/ethanol (10/90 wt%); T=30°C.

In order to understand the transport phenomena through these filled membranes better, the results have been modelled as described in the following section.

II.5- Modelling

II.5.1- Development of the model

The model used in our study was developed by te Hennepe et al. [10] for the pervaporation of alcohol/water mixtures by means of silicalite-1 filled silicone rubber membranes. Here only the final equation will be given.

However it must be said that the geometric factor which was determined for silicalite-1 particles is not the same as that for active carbons. In the case of silicalite-1, the particles could be considered as cubic whereas the carbon particles used in our study do not have a very well determined shape, which makes the estimation of this parameter difficult. As a first estimate the same value was used as for silicalite-1.

The equation for the pure component flux J_i, is:

$$J_i = \Delta p_i \Bigg/ \left(\frac{(1 - \phi_c^{1/3})\, d}{P_{r,i}} + \frac{3/2\, \phi_c^{1/3}\, d}{P_{r,i}\,(1 - \phi_c) + 3/2\, P_{c,i}\, \phi_c} \right) \qquad (1)$$

in which:

J_i : flux of pure component i ($g.m^{-2}.h^{-1}$)
p_i : partial pressure gradient of species i across the membrane (mmHg)
ϕ_c : volume fraction of carbon in the membrane (-)
d : thickness of the membrane (m)
$P_{r,i}$: rubber permeability for component i ($g.m.m^{-2}.h^{-1}.mmHg^{-1}$)
$P_{c,i}$: carbon permeability for component i ($g.m.m^{-2}.h^{-1}.mmHg^{-1}$)

$P_{r,i}$ is determined from pervaporation data with unfilled membranes. In this case, equation 1 is reduced to:

$$J_i = \Delta p_i \frac{P_{r,i}}{d} \qquad (2)$$

The value of $\Delta p_i = (p_{i,\text{feed side}} - p_{i,\text{permeate side}})$ is calculated by assuming $p_{i,\text{permeate side}} = 0$ (vacuum at the downstream side of the membrane) and with equation (3) for $p_{i,\text{feed side}}$:

$$p_{i,\text{feed side}} = c_{i,\text{feed side}} \cdot \gamma \cdot p_i^{o} \ \text{(mmHg)} \qquad (3)$$

where:

$c_{i,\text{feed side}}$: concentration in the liquid feed mixture (mole fraction)
γ : activity coefficient calculated from the Margules equation
p_i^{o} : calculated from the Antoine equation

The model implicitly assumes that both rubber and adsorbent permeabilities are independent of the adsorbent content of the membrane. For more details about the model one is referred to [10] and chapter VI of this thesis.

II.5.2- Results

Fitting equation (2) to the results obtained with pure EPDM, the following values are found:

$$P_{r,\text{toluene}} = 672.3\ 10^{-6}\ g.m.m^{-2}.h^{-1}.mmHg^{-1}$$
$$P_{r,\text{ethanol}} = 10.2\ 10^{-6}\ g.m.m^{-2}.h^{-1}.mmHg^{-1}$$

These two values are used in equation (1) to determine $P_{c,\text{toluene}}$ and $P_{c,\text{ethanol}}$.

Two different carbons were considered: CP and SX Ultra. They were chosen because of their large porous volumes (see table 1). The same model was also applied to the results obtained with the zeolite NaY with a ratio Si/Al of 20. The adsorbent permeability was taken as a variable to fit the calculated fluxes

J_i to the experimental data. The results are given in figures 5 to 7.

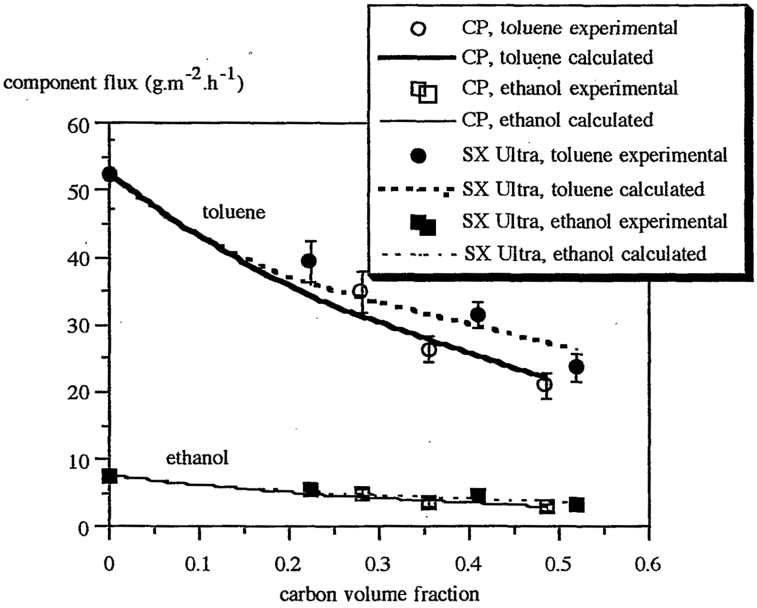


Figure 5: Experimental and calculated component fluxes for CP and SX Ultra filled EPDM membranes.

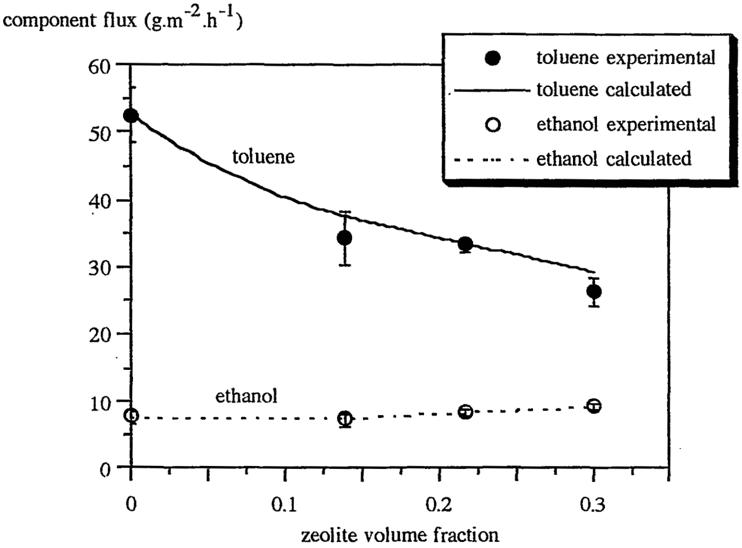


Figure 6: Experimental and calculated component fluxes for NaY 20 filled EPDM membranes.

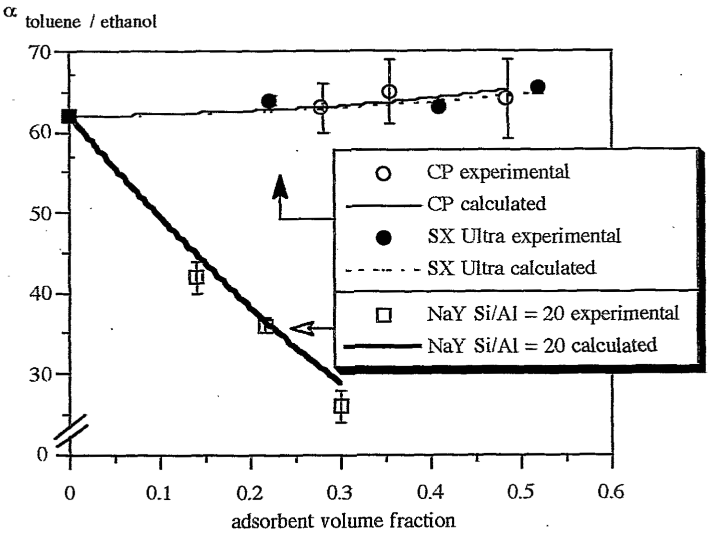


Figure 7: Experimental and calculated selectivity for filled EPDM membranes.

A very satisfactory agreement can be observed between the experimental data and the model fit. The fitting parameters are given in table 6.

Permeability coefficient	CP	SX Ultra	NaY Si/Al=20
$P_{i,toluene}$ $(g.m.m^{-2}.h^{-1}.mmHg^{-1})$	$27.8.10^{-6}$	$165.2.10^{-6}$	0
$P_{i,ethanol}$ $(g.m.m^{-2}.h^{-1}.mmHg^{-1})$	0	$2.1.10^{-6}$	$29.4.10^{-6}$

Table 6: Toluene and ethanol permeabilities of various adsorbents.

II.5.3- Discussion

The permeability values obtained confirm that the active carbon CP is essentially impermeable to toluene and ethanol in comparison with the polymer phase EPDM. In the case of SX Ultra, the permeabilities are roughly a factor 4 lower than those of EPDM. The reason for such a behaviour is the morphology of the pores inside the particles. One can imagine that if the pores are not interconnected, there is no pathway from one side of a particle to the other. Hence the sorbed molecules will not diffuse out and the particles just act like immobilizing sites for the permeant. The results suggest that SX Ultra exhibits a somewhat more interconnected structure than CP.

On the other hand, the pervaporation results obtained with the zeolite NaY with a Si/Al ratio of 20 can be explained by an ethanol selective permeation behaviour, though the adsorption experiments revealed a selective character slightly in favour of toluene. A molecular sieving effect by size exclusion must then be the mechanism involved, i.e. the large toluene molecules (kinetic diameter 6.5 Å) diffuse much slower than the ethanol molecules (kinetic diameter 4.5 Å). The final result is a decrease of the toluene flux and an increase of the ethanol flux, thus a decrease of the selectivity for toluene. For this adsorbent, the porous structure is open and this allows the molecules to diffuse from one side of the particles to the other. The same mechanism can be used to explain the experimental results obtained with silicalite-1 (figure 4).

However, the "zeolite permeabilities" given in table 6 should not be considered as intrinsic properties of the zeolite. They are characteristic of one zeolite in one polymer phase and in the *experimental conditions of the present study*. This will be discussed more in detail in chapter VI of this dissertation.

II.6- Conclusions

In the pervaporation of toluene/ethanol mixtures active carbons incorporated into various polymer phases do not result in an improvement of the selectivity for toluene. Furthermore, the total flux decreases drastically with increasing amount of active carbons and the effect of using a variety of porous structures cannot be established. This is due to the closed pore structure of the carbons. It means that even a highly selective adsorption for toluene by the active carbon has no influence on the selectivity when used in a membrane.

The results clearly indicate that an open pore active carbon has to be used. In principle such kind of material can be produced by pyrolysis of polymers (polyvinylidene chloride for instance [19,20]) to form a carbon molecular sieve membrane.

The effect of open pore zeolites like NaY 20 is quite different. A molecular sieving of toluene is observed in this case, whereas ethanol diffuses through the zeolite pores.

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III

ADSORBENT FILLED POLYMERIC MEMBRANES FOR GAS SEPARATION

Part 1: Improvement of the gas separation properties of polymeric membranes by incorporation of microporous adsorbents

Summary

The effect of the introduction of specific adsorbents on the gas separation properties of polymeric membranes has been studied. For this purpose both carbon molecular sieves and zeolites are considered. The results show that zeolites such as silicalite-1, 13X and KY improve the separation properties of poorly selective rubbery polymers towards a mixture of carbon dioxide/methane to a large extent. Some of the filled rubbery polymers achieve intrinsic separation properties comparable to cellulose acetate, polysulfone or polyethersulfone. However, zeolite 5A leads to a decrease in permeability and an unchanged selectivity. This is due to the impermeable character of these particles, i.e. carbon dioxide molecules cannot diffuse through the porous structure under the conditions applied. Using silicalite-1 also results in an improvement of the oxygen/nitrogen separation properties which is mainly due to a kinetic effect.

Carbon molecular sieves do not improve the separation performances or to a very small extent. This is caused by a mainly dead-end (not interconnected) porous structure which is inherent to their manufacturing process.

III.1- Introduction

Adsorbents such as zeolites and molecular sieving carbons are well known for the separation of gaseous mixtures by Pressure Swing Adsorption. This process involves the use of the specific microporous adsorbents in a semi-continuous way with sorption-desorption cycles, making use of different rates of sorption or different equilibrium uptakes. In the present study, the adsorbents have been incorporated into a polymeric matrix to form a heterogeneous membrane. In filled membranes the selective properties of the specific adsorbents are used in a continuous way.

Such a concept was already shown to improve the separation properties of polymers for pervaporation [1,3] and gas separation [2]. In the case of pervaporation of ethanol/water mixtures using silicone rubber membranes, both the ethanol selectivity and the permeability were enhanced by the incorporation of silicalite-1 particles into the polymer matrix [1]. The same type of membranes showed improved gas separation properties [2]. However these studies were limited to one type of zeolite or one polymeric phase. The present paper aims at giving a larger overview of the influence of various zeolites and molecular sieve carbons on the gas separation properties of polymer materials. Therefore four zeolites with different hydrophilic/hydrophobic properties and various pore sizes were incorporated into five different polymers.

III.2- Basic properties of zeolites and carbon molecular sieves

III.2.1- Zeolites

It is beyond the scope of this paper to give an extended and detailed description of the microporous adsorbents considered (see chapter I and review articles [4-7]). However some basic characteristics which are of importance for the present study will be summarized briefly.
Zeolites are crystalline alumino-silicates composed of AlO_4 and SiO_4 tetrahedra, which build up a network of channels and cavities. The microcrystalline voids and channels which are interconnected are responsible for the very specific properties of these adsorbents. The aperture size is typically in the range of molecular dimensions, i.e. 3 to 10 Å. The aluminum atom is trivalent, and therefore an excess of negative charge is introduced in the network when Si is replaced by Al in the tetrahedra. This charge is compensated by non-framework cations, located near the negative charges; the most common ones are Na^+, K^+ and Ca^{++}. The number of cations is thus determined by the number of aluminum atoms in the framework. Because of the presence of cations, these zeolites are polar adsorbents. This means that molecules such as water, ammonia (strong dipoles), carbon dioxide, nitrogen (quadrupolar) and aromatic hydrocarbons (π layer interaction) are adsorbed more strongly than non polar species of comparable molecular weight. Zeolites with a high ratio Si/Al are hydrophobic and the adsorption is mainly governed by van der Waals forces.

Therefore four main factors influence the properties of a zeolite:

- pore size which acts on the ability of a molecule to enter and diffuse through the zeolite framework.
- ratio Si/Al which determines the number of cations and thus the hydrophilicity of the zeolite framework.
- type of cation (valence and size).
- direction of the pores (1, 2 or 3D porous network).

Some applications of zeolites in the separation of gaseous mixtures are the dehydration of industrial gases using hydrophilic zeolites, the separation of air by preferential equilibrium sorption of nitrogen or the removal of H_2S from sour gas [4].

III.2.2- Carbon Molecular Sieves

Carbon Molecular Sieves (CMS) are characterized by a pore size distribution which is much narrower than in the case of common active carbons [7,8]. It means that, contrary to zeolites, carbon molecular sieves cannot be given a definite pore size but a mean pore size which is in the range of molecular dimensions. Furthermore, their internal surface is essentially hydrophobic, with possible variations due to acidic surface groups [9]. Carbon molecular sieves are industrially used to separate air by adsorption of oxygen and also to remove carbon dioxide from landfill gas [10].

III.3- Experimental

III.3.1- Adsorbents

The adsorbents considered are the zeolites 5A (Ceca S.A., France, crystal density: ρ_c=1.48 g/cm^3), silicalite-1 (UOP, USA, ρ_c=1.76 g/cm^3), KY (Ceca S.A., ρ_c=1.52 g/cm^3), 13X (Ceca S.A., ρ_c=1.54 g/cm^3) and the carbon molecular sieves Cecalite (Ceca S.A), Carbosieve (Supelco Separation Technologies, USA) and W20 (Norit N.V., The Netherlands). Furthermore, non porous silica (Sigma) was used as inert filler (N_2 BET surface area: 5.8 m^2/g). The zeolites were activated in air at 350°C for two hours except for silicalite-1 where an activation temperature of 500°C was applied (calcination of the template used during synthesis). The crystallinity of the zeolites was examined by X-ray powder diffraction. The size of the zeolite particles was typically in the range of 1 to 5 µm.

The carbons were activated in a vacuum oven at 150°C for 24 hours. The adsorbents were then kept in a vacuum oven at room temperature. Table 1 (and table 4 in the appendix to this chapter) gives some basic properties of these microporous adsorbents.

zeolite	pore size (Å)	Si / Al	cation	directions	pore volume (cm^3.g^{-1})
5A	4.3	1	Na^+ / Ca^{++}	3D	0.28
silicalite-1	5.3*5.6<->5.1*5.5	∞	-	2D	0.19
KY	7.4	2.6	K^+	3D	-
13X	7.4	1.2	Na^+	3D	0.36

Table 1: Main characteristics of the zeolitic adsorbents; kinetic diameters of the gases used are: CO_2 3.3 Å, CH_4 3.8 Å, O_2 3.46 Å, N_2 3.64 Å.

III.3.2- Polymers

Polydimethylsiloxane (PDMS, RTV 615 A and B, General Electric), Ethylene-propylene rubber (EPDM, Keltan 578, DSM), polychloroprene (PCP, Aldrich), and Nitrile Butadiene rubbers (Polysar) with two different amounts of acrylonitrile segments: 45%, Krynac 45.50 (NBR 45) and 50%, Krynac 50.75 (NBR 50) were used as polymer.

III.3.3- Membrane preparation

Membranes were prepared by dispersion of the adsorbent phase in the polymeric solution, followed by a casting-evaporation process. Hexane and chloroform were used as solvents. The evaporation step was carried out first overnight under a nitrogen stream, then in a vacuum oven at 30°C for at least 24 h. The membranes thus obtained were 50 to 200 µm thick. The homogeneous dispersion of the particles was observed by Scanning Electron Microscopy (figure 1), using a JEOL JSM-T 220A Scanning Microscope.

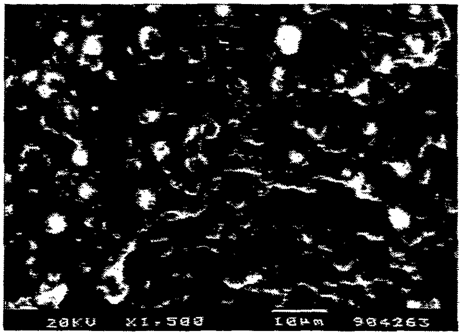

Figure 1: Cross-section of a PDMS membrane filled with 60wt% of zeolite 5A (X 1500).

III.3.4- Equipment and methods

The gas separation properties were determined by means of an automized set-up with a mixture of carbon dioxide and methane (25/75 vol%), pure oxygen and pure nitrogen at room temperature (24°C). The low pressure side was kept under vacuum (10^{-2}-10^{-1} mbar) while the feed pressure was set at 5.3 bars. The permeate flux was determined by measuring a pressure increase in a calibrated volume, the permeate pressure remaining negligible compared to the feed pressure. The permeabilities are expressed in Barrer with 1 Barrer = 10^{-10} $cm^3(STP).cm.cm^{-2}.s^{-1}.cmHg^{-1}$. The selectivity was calculated from the gas chromatographic analyses of the feed mixture and the permeate in the case of CO_2/CH_4, and from the ratio of the pure gas permeabilities in the case of O_2/N_2. For more details about the experimental set-up, see reference [11] and appendix 1 to this dissertation. The permeation experiments were carried out until steady-state was reached, which means from 1 to 5 days depending on the zeolite considered. The gas sorption experiments were carried out with a pressure-decay set-up, as described in appendix 1 and references [12] and [13]. The membrane samples were evacuated at 30°C at 10^{-3} mbar for at least 15 hours before measurement, in addition to the normal treatment. The experiments were carried out at 30°C.

III.4- Results and discussion

III.4.1- Gas permeation using carbon molecular sieve filled membranes

The results obtained with carbon molecular sieves are given in the appendix to this chapter.

III.4.2- Gas permeation using zeolite filled membranes

Carbon dioxide/methane

The open microporous structure of the zeolites results in an increase both in selectivity and permeability for carbon dioxide over methane in the case of silicalite-1, KY and 13X, as can be seen in figure 2 (a and b).
Here EPDM was used as polymeric phase. The improvement of the separation properties becomes more pronounced when the volume fraction of zeolite in the polymer matrix increases, until the amount of adsorbent in the membrane surpasses an optimum. This results in the formation of non selective voids as can be seen from the large increase in permeability and decrease in selectivity. This occurs when the volume fraction of zeolite is in the range of 45 to 55 percent (figure 2).

The largest improvement in selectivity and permeability for carbon dioxide was obtained by using zeolite KY (see figure 2), for which the pore size is about twice the kinetic diameters of carbon dioxide and methane (which are 3.3 and 3.8 Å respectively). Zeolite 13X, which has basically the same pore size but a lower Si/Al ratio, gave results comparable to silicalite-1 which pore size is 5.5 Å.

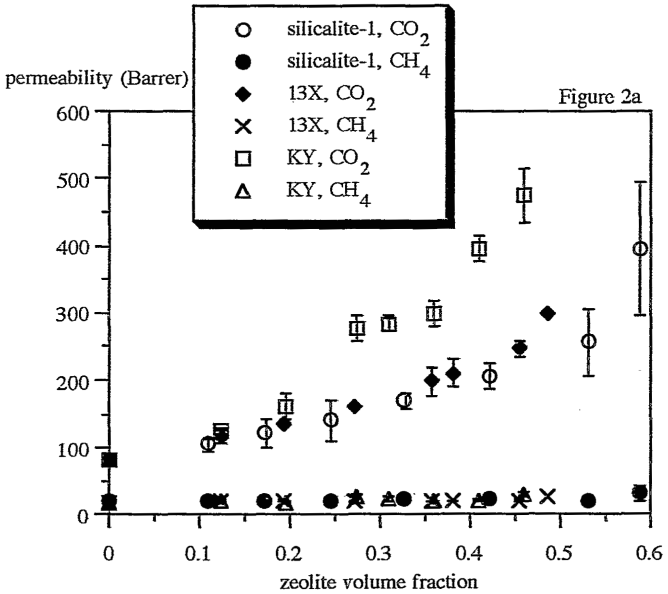

Figure 2a: Effect of filling for the zeolites silicalite-1, 13X and KY on the CO_2/CH_4 separation properties of EPDM (a: permeabilities, b: selectivity); 1 Barrer=10^{-10} cm^3(STP).cm.cm^{-2}.s^{-1}.$cmHg^{-1}$.

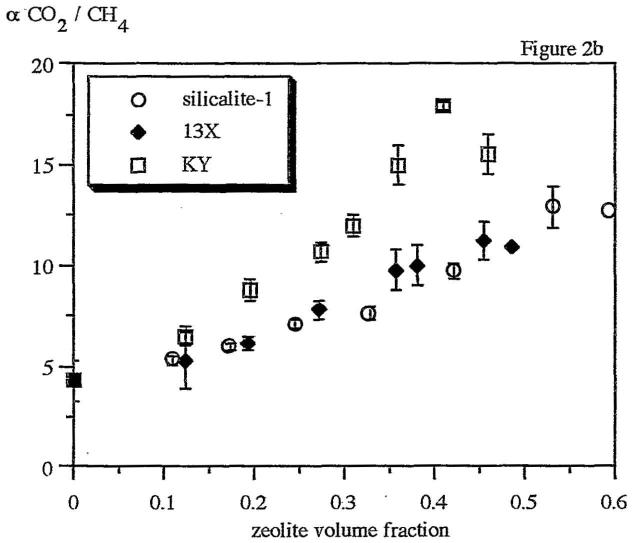

Figure 2b: Effect of filling for the zeolites silicalite-1, 13X and KY on the CO_2/CH_4 separation properties of EPDM (a: permeabilities, b: selectivity); 1 Barrer=10^{-10} cm^3(STP).cm.cm^{-2}.s^{-1}.$cmHg^{-1}$.

Opposite to the first three zeolites considered, zeolite 5A does not enhance the membrane performance (table 2), despite the fact that the pore size (4.3 Å) is large enough to fit to the kinetic diameters of the gas molecules.

membrane	P_{CO_2} (Barrer)	α_{CO_2 / CH_4}
PDMS	2920	2.7
PDMS + 50 wt% 5A	1800	2.8
PDMS + 28 wt% silica	2407	2.8
PDMS + 59 wt% silica	1910	3.0
EPDM	81	4.3
EPDM + 52 wt% 5A	65	4.4
EPDM + 62 wt% 5A	50	4.5
EPDM + 40 wt% silica	72	4.5
EPDM + 53 wt% silica	55	4.6

Table 2: Effect of zeolite 5A and non-porous silica on PDMS and EPDM separation properties; 1 Barrer=10^{-10} cm^3 (STP).cm.cm^{-2}.s^{-1}.$cmHg^{-1}$.

The properties are similar to those of non porous silica with respect to the effect on the gas permeation properties (see table 2). This means that the porous structure of zeolite 5A is not open for the permeation of gas molecules in the particular conditions encountered in the polymer matrix. Possible reasons for this phenomenon will be discussed later.

From the obtained results it can be concluded that molecular sieving by size exclusion is not the only mechanism involved and that the affinity of the gas molecules for the zeolite internal surface also plays a major role.

Screening the results of a series of polymers shows that the zeolites silicalite-1 and KY are able to increase significantly their separation properties. Especially for a polymer which selectivity is about 15 for carbon dioxide/methane the results of the filled membranes are comparable to those of industrially used polymer membrane materials (cellulose acetate, polysulfone) as can be seen in figures 3 a and b and figure 4.

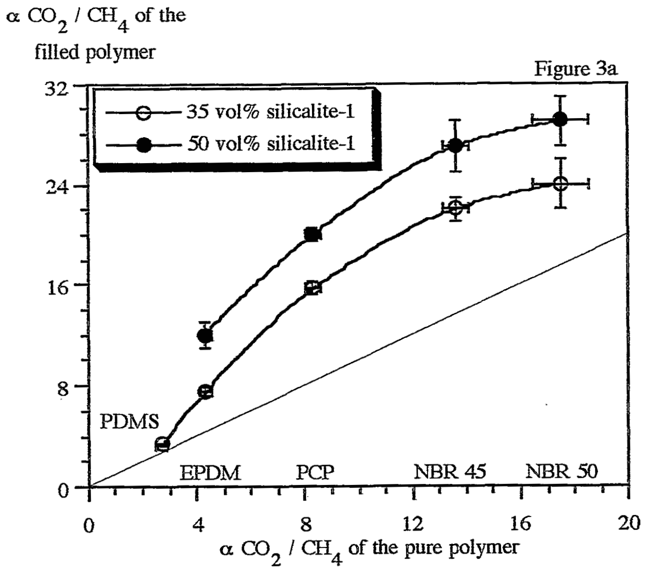

Figure 3a: Effect of the zeolites silicalite-1 (a) and KY (b) on the CO_2/CH_4 selectivity of various rubbery polymers.

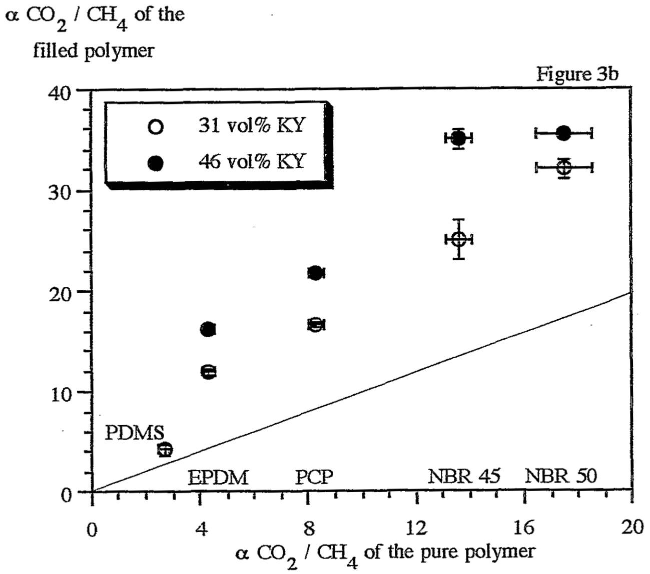

Figure 3b: Effect of the zeolites silicalite-1 (a) and KY (b) on the CO_2/CH_4 selectivity of various rubbery polymers.

In these figures the diagonal lines indicate the results if the zeolites had no effect on the separation properties of the different polymers. All polymers showed improved selectivity and permeability for carbon dioxide when filled with silicalite-1 or KY, despite the fact that for the polymers studied the permeabilities ranged from about 3 (NBR 50) to 3000 Barrer (PDMS) and their selectivities from 2.7 (PDMS) to 17.5 (NBR 50). For example, the addition of 50 volume percent of silicalite-1 to NBR 50 gives a material with a selectivity of 29 and a permeability of 7 Barrer. NBR 45 filled with 46 volume percent of zeolite KY results in a material with a selectivity of 35 and a permeability of 14 Barrer for carbon dioxide.

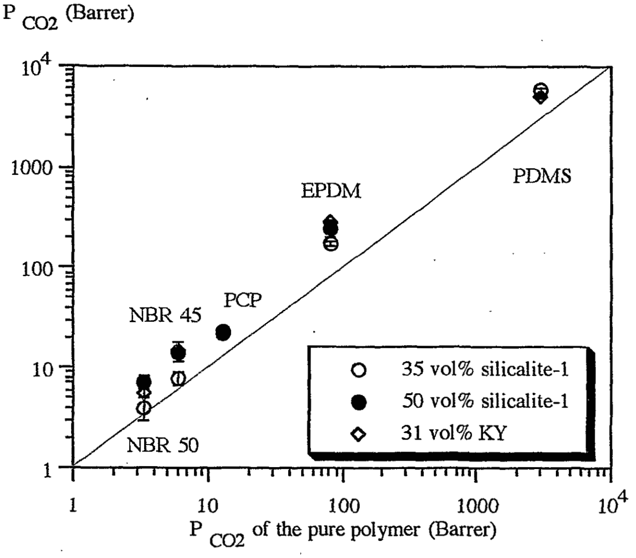

Figure 4: Effect of the zeolites silicalite-1 and KY on the CO_2 permeability of various rubbery polymers; 1 Barrer=10^{-10} cm^3 (STP).cm.cm^{-2}.s^{-1}.$cmHg^{-1}$.

Figures 3 and 4 also show that filling with zeolite KY always results in a larger improvement of the CO_2 selectivity and permeability compared to silicalite-1 for a given volume fraction in a given polymer. This is in agreement with the observations for the single polymer EPDM when using different volume fractions. Silicalite-1 and type Y zeolite both show a sorption selectivity towards CO_2 [7,14], but the selectivity obtained with Y (NaY in reference [14]) is much larger, due to its hydrophilic surface. It may be assumed that the same is observed when the sodium cations are exchanged for potassium, which would explain the beneficial influence of KY on the permeation properties.

This concept may also be applied to improve the separation performance of very selective (glassy) polymers. This was also investigated, but the obtained results were not that positive due to a very poor adhesion of the polymer matrix to the external surface of the zeolite, resulting in large voids between the polymer and the zeolite crystals. The incorporation of zeolites in glassy polymers is described elsewhere [23] and will not be considered here.

Oxygen/nitrogen

A very surprising effect was observed for the oxygen/nitrogen separation. Incorporation of silicalite-1 resulted in an increase in the ideal selectivity for oxygen in the case of poorly selective rubbery polymers (table 3). This was already observed for PDMS and our results are similar to literature [2]. The selectivity values obtained with EPDM as polymeric phase are comparable to intrinsic values of polymethylpentene or poly-dimethyl-phenylene oxide which are industrially used membrane materials for air separation.

membrane	P_{O_2} (Barrer)	P_{N_2} (Barrer)	α_{O_2/N_2}
PDMS	606	289	2.1
PDMS + 28 vol% silicalite-1	892	355	2.5
PDMS + 37 vol% silicalite-1	998	373	2.7
PDMS + 47 vol% silicalite-1	1370	521	2.6
EPDM	16	5.3	3
EPDM + 32 vol% silicalite-1	29	7.5	3.9
EPDM + 53 vol% silicalite-1	40	8.5	4.7

Table 3: Effect of silicalite-1 on O_2/N_2 separation properties of PDMS and EPDM; 1 Barrer=10^{-10} cm^3 (STP).cm.cm^{-2}.s^{-1}.$cmHg^{-1}$.

Silicalite-1 shows a sorption selectivity for carbon dioxide over methane (separation factor: 2.7 at 25°C [8,14]) but no significant equilibrium sorption selectivity for oxygen over nitrogen is reported for this zeolite [15]. The improvement in selectivity obtained for the filled membranes is mainly determined by a kinetic effect, i.e. the oxygen molecules can diffuse faster through the porous structure of silicalite-1 than the nitrogen molecules. This is comparable to what is observed with carbon molecular sieves which have almost no equilibrium sorption selectivity for oxygen but are nevertheless used in Pressure Swing Adsorption. Here the separation of air is based on a faster sorption rate of oxygen over nitrogen [16]. Such a kinetic selectivity towards oxygen is also observed with zeolite 4A (pore size: 3.8 Å), which is even sorption selective towards nitrogen at equilibrium [17]. It should be noticed that silicalite-1 also enhances the nitrogen permeability with the polymers investigated, but this was not observed for methane.

III.4.3- Gas sorption isotherms

Carbon dioxide sorption isotherms show that the presence of zeolite particles in the membrane matrix enhances the carbon dioxide sorption capacity to a large extent (see figure 5).

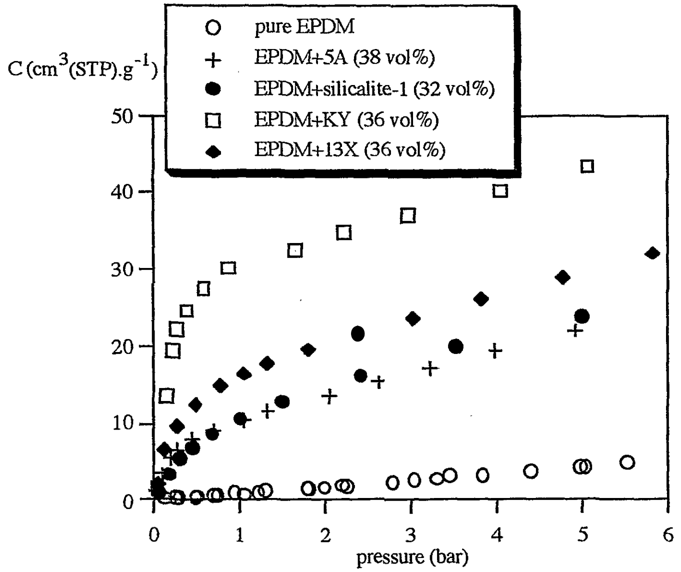

Figure 5: Carbon dioxide sorption isotherm of pure and zeolite filled EPDM; T=30°C.

However, when considering transport properties the sorbent should not only sorb the gas molecules, but also should allow these to diffuse under the driving force applied. This is indeed what is observed for silicalite-1, KY and 13X. On the other hand zeolite 5A also enhances the sorption capacity of EPDM, but not the gas permeation properties (table 2). This means that the sorbed gas molecules cannot diffuse through the zeolite porous structure but are trapped into the matrix and exhibit a very low mobility. There may be two reasons for this behaviour. The first one is that under permeation conditions, the gas molecules are very strongly bound to the sorption sites and cannot desorb (the heat of sorption of carbon dioxide in type A zeolite is larger than in type Y or in silicalite-1 [14]); therefore they block the way for other molecules. The second reason is that water of hydration remains in the zeolite structure and cannot be removed by vacuum activation at room temperature (a high temperature would degrade the polymeric phase). The latter explanation is more likely to be correct since 5A is a very hydrophilic zeolite with a high affinity for water resulting in a lower CO_2 sorption capacity than expected from pure zeolite sorption data [18]. Moreover, Paul and Kemp [18] showed that activation of a 5A filled silicone rubber membrane at 200 °C prior to use does not make zeolite 5A beneficial for gas permeation, i.e. the permeability of the membrane is lowered and the diffusion time-lag drastically enhanced. Therefore even in-situ activation does not make much difference with respect to the permeation results. In addition, it can be seen from the sorption isotherms that the zeolite resulting in the largest improvement of carbon dioxide sorption capacity (KY, see figure 5) also leads to the largest improvement of the carbon dioxide permeability and selectivity. Zeolite 13X gives a surprisingly low increase of the sorption capacity when considering its microporous volume and low ratio Si/Al. These two factors should favour the sorption of carbon dioxide to a much larger extent than in the case of the hydrophobic silicalite-1 (Si/Al=∞). Here again the presence of water of hydration might play a decisive role. After the thermal activation and storage in the vacuum oven, it may be assumed that mostly all the water has been removed from the crystal structure. However, the preparation of the membrane and the gas separation experiments themselves involve water traces which will adsorb into the zeolite structure more preferentially than carbon dioxide. This effect can decrease the sorption capacity to a substantial extent (like in the case of 5A) which reduces the ability to improve the gas permeation properties. Despite this, some improvement was observed with respect to CO_2/CH_4 permeation which can be attributed to the large pores present in 13X which are able to accomodate both carbon dioxide and water traces without blocking the diffusion path completely.

III.5- Conclusions

The carbon dioxide/methane separation performances of rubbery polymers are significantly enhanced when zeolites are incorporated which are carbon dioxide sorption selective, provided that the gas molecules can diffuse through the zeolite particles. This is the case when zeolites like silicalite-1, KY and 13X are considered, leading to separation properties which are comparable to commonly used glassy polymer membrane materials. This effect is polymer independent and is even observed when non-selective or poorly permeable polymers are considered. However, zeolite 5A, which seems suitable as sorbent because of its pore size and hydrophilic character, does not show the same positive enhancement.

Furthermore, silicalite-1 was found to be beneficial to the oxygen/nitrogen separation properties of silicone rubber (PDMS) and Ethylene-propylene rubber (EPDM) despite its non-selective equilibrium sorption properties.

Finally, carbon molecular sieves do not lead to any significant improvement of the gas separation properties of rubbery polymers due to a dead-end porous structure. This latter result is further described in the appendix to this chapter.

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Appendix to chapter III

Investigation of carbon molecular sieves as filling material

As indicated previously, carbon molecular sieves were also investigated with respect to their effect on the gas separation properties of rubbery polymers. Table 4 gives some properties of the carbon molecular sieves used. It can be seen that a significant part of the porous volume consists of micropores (diameter < 20 Å).

	mean micropore size (Å)	microporous vol. ($cm^3.g^{-1}$)	total porous vol.($cm^3.g^{-1}$)
Cecalite	6-7	0.18	0.52
W20	-	0.22	0.55
Carbosieve	5-7	-	-

Table 4: Main characteristics of the carbon molecular sieves (data from manufacturers).

Table 5 gives some gas permeation results obtained with filled membranes using carbon molecular sieves.

membrane	P_{CO_2} (Barrer)	α_{CO_2 / CH_4}	P_{O_2} (Barrer)	α_{O_2 / N_2}
PDMS	2920	2.7	606	2.1
PDMS + 40 wt% W20	3170	3.35	-	-
EPDM	81	4.3	16	3
EPDM + 30 wt% W20	93	4.8	-	-
EPDM + 45 wt% Cecalite	55	5.2	13	4.3
EPDM + 50 wt% Carbosieve	120	8	23	4.3

Table 5: Gas separation properties of membranes filled with carbon molecular sieves; 1 Barrer=10^{-10} cm^3 (STP).cm.$cm^{-2}.s^{-1}.cmHg^{-1}$.

It can be seen that in the case of CO_2/CH_4 separation no improvement is observed with respect to the properties of PDMS and EPDM, except for Carbosieve. This lack of transport improvement is mainly due to a dead-end porous structure, i.e., pores going from the outside to the inside of the particles without being interconnected. Therefore the gas molecules cannot diffuse through the carbon particles, or to a very small extent. To understand the origin of such a porous structure better, one must think of the way carbon molecular sieves are manufactured [7,8]. Though the manufacturing processes are carefully kept secret, it is conjectured that the preparation is based on hard-coal gasification in air followed by a treatment to control the pore structure. This is achieved either by cracking hydrocarbons within the micropore system, resulting in a partial blocking of the pore mouths [19,20,], or by mild steam activation which

results in an enlargement of the pores.
Both ways result in a macroporous structure from which micropores are developed without interconnections. The selective pores are thus mostly dead-end pores which are effective for use in a Pressure Swing Adsorption process, but not when included into a membrane matrix for a continuous application. Therefore, the applicability of carbon molecular sieves as filling material in a polymer matrix for separation purposes requires an open structure which seems strongly dependent on the method of preparation.

It can be concluded that carbon molecular sieves cannot compete with zeolites as filling material in polymeric membranes for gas separation. The use of a genuinely molecular sieve carbon membrane seems more promising, as described in literature by Koresh and Soffer [21,22].

IV

ADSORBENT FILLED POLYMERIC MEMBRANES FOR GAS SEPARATION

Part 2: Influence of the intrinsic zeolite properties on the gas permeation behaviour of filled membranes

Summary

The intrinsic properties of zeolites have been investigated with respect to their effect on the gas permeation properties of the zeolite filled membranes. The zeolite characteristics investigated are the pore size, the pore directions, the ratio Si/Al and the type of cation present in the structure. It is shown that there is no direct relation between the pore size and the kinetic diameters of the molecules to be separated, i.e. the zeolites with larger pores result in the best improvement of the CO_2/CH_4 separation properties. Furthermore, zeolites with an unidirectional pore system have a very limited effect on the permeation results. The zeolite Offretite incorporated into the polymer phase without prior calcination does not result in any improvement. This is due to the template molecule employed during synthesis which is still present in the porous structure, showing that the transport actually occurs through the pores and not by surface diffusion at the external surface of the zeolite particles.
With zeolites ZSM-5 and Faujasite, the influence of the Si/Al ratio is studied and an effect is observed at low Si/Al ratios. Finally, the influence of the cation present in the zeolite porous system is investigated with respect to gas permeation, showing that bivalent cations hinder the transport of gas molecules through the zeolite pores.

IV.1- Introduction

In a previous publication [1, see also chapter III], the effect of the incorporation of common zeolites on the gas separation properties of rubbery polymers was investigated, showing that a large improvement of the separation properties can be achieved both in selectivity and permeability.
This chapter aims at studying the influence of the zeolite properties on the membrane separation characteristics more precisely. There are four main factors influencing the zeolite sorption and diffusion properties, as already mentioned in chapters I and III:

- the pore size which affects the ability of a penetrant molecule to enter and diffuse through the zeolite framework.
- the ratio Si/Al which determines the number of cations and thus the hydrophilicity of the zeolite framework.
- the type of cation (size and valence).
- the direction of the pores (1, 2 or 3D porous network).

These four factors have been investigated by using zeolites with various porous structures, chemical compositions and cations. However, it must be noticed that it is rather difficult to study each of these factors independently because they are more or less related to each other. Hence, it is not possible to investigate the influence of the pore size without changing either the chemical composition of the zeolite or the dimensionality of the network.
Furthermore the pre-treatment of the zeolite (activation conditions) is also considered as a possible factor influencing the gas permeation results.

IV.2- Experimental

IV.2.1- Materials

The zeolites were activated and handled as usual (see chapter III) except for certain cases in which the activation conditions were varied (mentioned when occuring). All zeolites were obtained from CECA S.A. (France) and the Groupement de Recherches de Lacq (Elf Aquitaine, France), except for Mordenite (PQ Zeolites B.V., Netherlands).
Zeolite Theta-1 was synthesized according to the procedure given in appendix 1 to this chapter. The various ion exchanged X and Y zeolites were prepared according to experimental methods described in the same appendix.
The polymers investigated in this chapter are polydimethylsiloxane (PDMS, RTV 615 A and B, General Electric), Ethene-propene rubber (EPDM, Keltan 578, DSM) and Nitrile-Butadiene Rubber (NBR, Krynac, Polysar). For more information see chapter II and appendix 3 to this thesis.
The membranes were prepared in the standard way (see chapter III).

IV.2.2- Measurement methods

The gas permeation and sorption experiments were carried out in the same way as described elsewhere (see [1] and appendix 1 to this thesis).
The chemical composition of the various zeolites was determined by elemental analysis using X-ray fluorescence (Philips PW 1480 X-ray spectrometer), Atomic Absorption Spectroscopy (AAS, Perkin Elmer 5000) and Thermal Element Analysis (Elemental Analyser Mod.1106, Carlo Erba-Strumentazione).

IV.3- Effect of the porous structure

IV.3.1- Pore size

As has been shown in reference [1] and chapter III of this thesis, the zeolite having the closest pore size to the kinetic diameter of the gas molecules to be separated does not necessarily lead to the best improvement in permeability and selectivity. The incorporation of zeolite 5A resulted in a constant selectivity and a decrease in permeability despite a pore size (4.3 Å) which was thought to be the most suitable among the zeolites investigated to separate carbon dioxide from methane (3.3 Å and 3.8 Å as kinetic diameters respectively). This was explained by a very slow diffusion of the carbon dioxide molecules through the zeolite pores. The results reported, however, only considered EPDM and PDMS as polymer phase.

In this section other polymers (NBR) are considered as well as other zeolites. In order to study the influence of the pore size only and draw conclusions, all the other properties of the zeolite should remain the same, i.e. pore direction and chemical composition. Thus a simple graph of a "facilitation factor" versus the pore size of the zeolite would not be of much significance.

Keeping the same porous network while changing the pore size is possible with type A zeolites. In this case, the cation determines the pore size, which means that the chemical composition is changing as well. Table 1 gives the results obtained with zeolites 3A, 4A and 5A. One can notice that all type A zeolites are totally ineffective in improving the selectivity of the rubbery polymers investigated. The reason for this behaviour is that the diffusion of the sorbed gas molecules from the zeolite to the polymer phase is very slow (it has been shown that the zeolite 5A (Ca^{++} exchanged) for instance does sorb carbon dioxide when incorporated into the membrane [1,12]). A similar behaviour is assumed to hold for the zeolite 4A (Na^+ exchanged, 3.8 Å) and the zeolite 3A (K^+ exchanged, 3.2 Å). It is known that these zeolites can only accomodate very small molecules like water. They are therefore used for the drying of industrial gases [11]. The diffusion of larger molecules (CO_2, CH_4) in the zeolite pores under the driving force applied during the gas separation experiments is therefore too slow to result in any improvement of the membrane separation properties.

membrane	P_{CO_2} (Barrer)	α_{CO_2/CH_4}
PDMS	2900	2.6
PDMS + 3A 37.6 vol%	1710	2.7
PDMS + 4A 40.1 vol%	1790	3.0
PDMS + 5A 40.8 vol%	1715	2.8
EPDM	81	4.3
EPDM + 4A 38.0 vol%	71	4.2
EPDM + 5A 27.1 vol%	76	4.3
EPDM + 5A 38.6 vol%	64	4.3
EPDM + 5A 49.2 vol%	45	4.3
EPDM + 5A (BDH Chemicals) 38.6 vol%	69	4.4
NBR 45	5.5	13.5
NBR 45 + 5A 38.0 vol%	4.7	7.3
NBR 50	3.3	17.5
NBR 50 + 5A 38.0 vol%	2.6	5

Table 1: CO_2/CH_4 separation properties of various membranes filled with zeolites 3A, 4A and 5A.

Incorporation of zeolite 5A into NBR results in a decrease of the permeability and of the selectivity. These experiments were carried out to investigate whether zeolite 5A is beneficial for relatively poorly permeable materials. It can be observed that this is not the case. The permeability of the filled membrane is lower than that of the unfilled polymer, as was already observed for the more permeable polymers EPDM and PDMS. One would expect a constant selectivity if the sorbed molecules do not diffuse out of the zeolite pores. However the measured selectivities are significantly lower than for the pure polymer. No explanation has yet been found for this phenomenon. Probably the same phenomenon occurs with EPDM and PDMS, but in these cases the contribution of the polymer phase is much larger, so that no change in selectivity is observed.

At last, zeolite 5A from another source (BDH Chemicals) was also investigated. Basically the same results are obtained as with the one originating from Ceca S.A., when incorporated into EPDM. This is a good indication that in the case of zeolite A, the type of zeolite determines the results and not a possible variation of the intrinsic properties from batch to batch.

IV.3.2- Pore directions

It is possible to find or prepare zeolites with different porous structures as described previously [2]. One interesting feature is the possibility to have pores forming a one-, two- or three-dimensional porous network. It may be clear that this parameter is very important in a membrane application, where once a molecule enters a pore, it has to diffuse all the way through the zeolite particle to reach the polymer phase again. Furthermore, in the case of a one-dimensional pore system the orientation of the zeolite particles relative to the driving force becomes critical.

Table 2 shows some results obtained with three different zeolites having characteristic porous networks: Theta-1, Mordenite and Offretite.

Zeolite Theta-1 has a strictly one-dimensional porous system with a pore size of 4.4x5.5 Å and a Si/Al ratio of 48 (hence Theta-1 is an organophilic adsorbent). Mordenite has a two-dimensional porous network with straight wide pores (6.5x7.0 Å) interconnected by narrow pores (2.6x5.7) and a Si/Al ratio of 6.7. However, in many cases this zeolite is considered as mono-dimensional because the second type of pores only allows the diffusion of very small molecules [3], at least at low Si/Al ratio. This is due to the blocking of the side pockets by the sodium ions [4]. The zeolite Offretite has a three-dimensional porous structure, with wide pores in one direction (6.7 Å) and narrow pores in the other two (3.6x4.9 Å) and a Si/Al ratio of 4.4 (see appendix 2 to this chapter for a more detailed description of these zeolites).

membrane	P_{CO_2} (Barrer)	α_{CO_2/CH_4}
EPDM	81	4.3
EPDM + Theta 15.8 vol%	89	4.4
EPDM + Theta 22.5 vol%	75	4.4
EPDM + Mordenite 33.6 vol% not activated	79	5.2
EPDM + Mordenite 33.6 vol% activated 2 hrs. at 300°C	80	4.6
EPDM + Mordenite 33.6 vol% activated 2 hrs. at 500°C	73	4.4
EPDM + Offretite 33.8 vol% not activated	77	4.3
EPDM + Offretite 33.8 vol% activated 2 hrs. at 300°C	133	8.9
EPDM + Offretite 33.8 vol% activated 2 hrs. at 500°C	212	13.8
EPDM + Offretite 33.8 vol% activated overnight at 500°C	245	15.2

Table 2: Effect of the pore dimensionality on the gas separation properties of zeolite filled EPDM.

Table 2 shows clearly that 1D (or pseudo 1D) systems (Theta-1, Mordenite) cannot improve the selectivity of EPDM, despite its low intrinsic selectivity. When a 1D porous network is used, it must be realized that when incorporated into a polymer matrix to form a membrane, approximately only one third of the particles will be oriented properly so that the pores are more or less in the direction of transport through the membrane. This means that only one third of the particles are really effective for transport. Furthermore, if one single defect is present in a 1D pore (plugging by impurities or by amorphous phase), the diffusing molecules are definitively blocked and no effect of the zeolite on the gas transport is to be expected at all.

In the case of zeolite Theta-1 the volume fraction of zeolite in the membrane is low since it was impossible to prepare leak free membranes with a larger amount of zeolite. Furthermore the zeolite was not 100% crystalline, which means that amorphous parts are still present. The zeolite consisted of clusters of very small particles which were not totally broken up by the membrane preparation procedure used in the study. These two factors might explain the somewhat high permeabilities and the constant selectivity.

Zeolite Mordenite hardly affects the separation properties of EPDM. The same argument as mentioned above holds, i.e. only one third of the particles are actually taking part in the transport mechanism. The selectivity is slightly increased but the permeability remains at the same level as that of the unfilled polymer. The activation conditions were also varied but it did not show much influence on the separation properties.

The experiments carried out with zeolite Offretite demonstrate the occurence of intraporous diffusion of the gas molecules. When not activated, this zeolite still contains the template cation (tetra methyl ammonium) necessary for the synthesis. The presence of this molecule was confirmed by the elemental analysis (appendix 2 to this chapter). When the zeolite is directly incorporated into the polymer phase, it does not improve the selectivity, and the permeability remains essentially constant. When the zeolite has been activated at moderate temperature (300°C, 2hrs.) it turns brown, indicating the deposition of carbon at the external surface. This carbon stems from the carbonization of the template molecules. Such a zeolite does increase the selectivity and the permeability of EPDM for carbon dioxide, despite the visible presence of some remaining carbon based molecules (table 3, appendix 2 to this chapter). If the zeolite is calcined at 500°C for another two hours it becomes white again, indicating that the template is mostly gone (confirmed by elemental analysis). A further activation at 500°C overnight ensures the complete removal of the template. In these two cases the zeolite results in a large improvement of the carbon dioxide selectivity and permeability (comparable to what was obtained with zeolite KY at equal volume fraction [1]). Figure 1 shows the CO_2/CH_4 separation properties of the Offretite filled EPDM membranes as a function of the degree of activation (the lines are just given to guide the reader's eye).

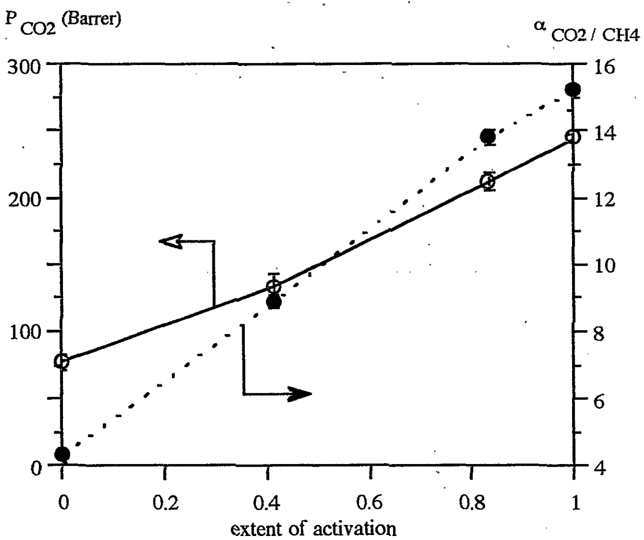

Figure 1: Influence of the extent of activation on the gas separation properties of Offretite filled EPDM membranes (33.8 vol% of zeolite); the extent of activation was calculated from the formula:
extent of activation = 1- (carbon weight % / carbon weight % non-activated);
the carbon content of the zeolites can be found in table 3, appendix 2 to this chapter.

This series of results shows that if the intracrystalline pores of the zeolite are blocked with molecules which are more or less fixed, no improvement of the gas separation properties is observed. This demonstrates that diffusion through the micropores is the determining mechanism as was already suggested by the results obtained with non-porous silica as filler (see reference [1] and chapter II). *Surface diffusion* at the *external* surface of the zeolite particles cannot be the mechanism involved.

IV.4- Effect of the chemical composition

IV.4.1- Effect of Si/Al ratio

To investigate the Si/Al ratio, two types of zeolites were selected:

- ZSM-5 (Si/Al=14.5), ZSM-5 (Si/Al=24.7), ZSM-5 (Si/Al=85), silicalite-1 (Si/Al=500).
- Faujasite: NaLSX (Si/Al=1), 13X (NaX, Si/Al=1.2), NaY (Si/Al=2.6), NaY (Si/Al=9.5), NaY (Si/Al=19.5).

In both cases the major counter ion is Na^+ and the pore size is maintained constant (the framework flexibility is neglected). In the Faujasite series, a zeolite X with a ratio Si/Al of 1 originally containing Ca^{++} as major cation was exchanged to a Na form (NaLSX, Low Silicium X). The exchange, however, is not complete. For more details about the chemical composition of all the zeolites, see appendix 2 to this chapter.

Figure 2 shows that the more aluminum atoms are present in the ZSM-5 framework, the larger is the carbon dioxide permeability. This can be explained by a more selective sorption of carbon dioxide at lower Si/Al ratio due to more polar properties with increasing aluminum content.

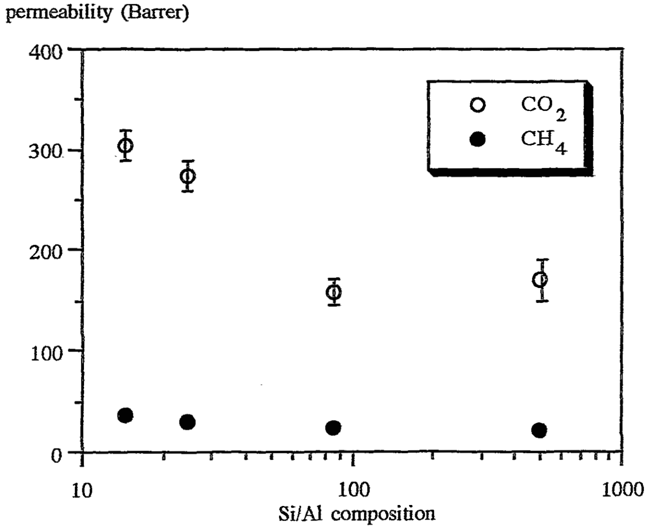

Figure 2: Effect of the Si/Al composition on the CO_2 and CH_4 permeabilities in the case of ZSM-5 filled EPDM membranes (32 vol% of zeolite).

The results obtained with Faujasite do not show the same clear trend (figure 3). There seems to be a maximum in the plot, which could mean that two effects are opposing each other. The first one is the same as described for ZSM-5: more aluminum in the framework makes the zeolite more hydrophilic and enhances the carbon dioxide sorption. However, too many cations in the structure might result in hindered diffusion of the gas molecules, which could explain the results observed with zeolite 13X (NaX, Si/Al=1.2) and NaLSX (Si/Al=1, 77% Na^+), i.e. a CO_2 permeability and a selectivity which are lower than with zeolite NaY. One must consider the result obtained with zeolite NaLSX carefully since this zeolite had not been fully exchanged. This means that some Ca^{++} cations remained in the structure which might add some hindrance (see following section).

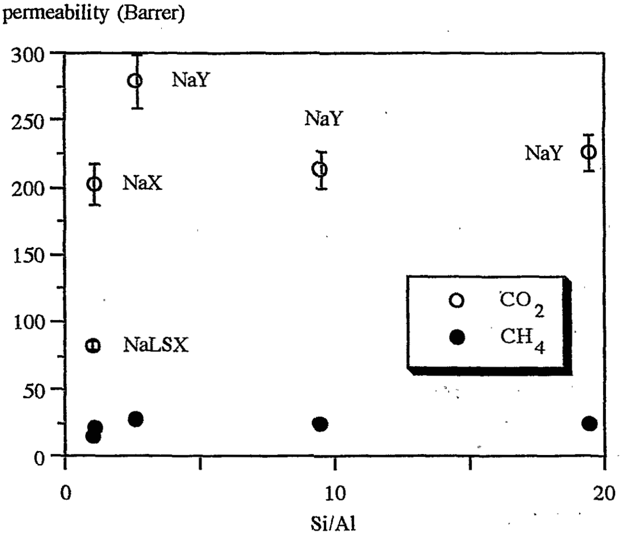

Figure 3: Effect of the Si/Al composition on the CO_2 and CH_4 permeabilities in the case of Faujasite filled EPDM membranes (38 vol% of zeolite).

IV.4.2- Effect of the cations

Zeolites containing aluminum atoms in their framework also include cations necessary to maintain the electroneutrality of the structure. The amount and the position of these cations depend on their nature, their valence and the amount of aluminum which is present in the zeolite network. The nature and location of the cations also influences the interaction of guest molecules with the zeolite structure [2,5-7]. The three following examples taken from literature illustrates these points.

Zeolite Y with sodium as cation has been reported to be sorption selective for meta-xylene in a mixture of meta- and para-xylene. On the other hand, zeolite KY is para-xylene selective [8]. This is explained by the higher polarizing effect of sodium compared to potassium, which favors the sorption of the most basic xylene (m-xylene). It was shown that the sorption enthalpies of the two xylenes are larger in NaY than in KY (meaning that the sorbed molecules are more strongly bound) and that $\Delta H_{m\text{-xylene}} > \Delta H_{p\text{-xylene}}$ in NaY whereas in KY $\Delta H_{m\text{-xylene}} < \Delta H_{p\text{-xylene}}$. This accounts for the reverse sorption selectivities. This paper also shows that the incorporation of bivalent cations in the zeolite framework (Ca^{++}, Ba^{++}) leads to a significant decrease of the loading capacity for xylenes.
Another significant example of the cation effect has been reported in reference [9]. The sorption enthalpies of carbon dioxide on zeolites CaY and CaX are larger than in the case of the corresponding NaY and NaX. This means again that the CO_2 molecules sorbed at a Ca-site are more strongly bound than at a Na-site.

The last striking example is the much larger ideal sorption selectivity of zeolite LiX for nitrogen over oxygen compared to zeolite NaX [10] (6 and 3 respectively at 1 atm and 298 K), though this phenomenon is not really explained yet.

One can imagine that the above mentioned factors are also of importance when zeolite filled polymeric membranes are considered .

In this section the Faujasite type of zeolite is considered (X and Y). It normally contains Na^+ as cation. Monovalent (Li^+, K^+) and bivalent cations (Ca^{++}, Ba^{++}) are considered to replace Na^+. Appendices 1 and 2 to this chapter give the ion exchange experimental procedures and the analysis results obtained.

The different zeolites were incorporated into EPDM and their CO_2/CH_4 separation properties were determined. Table 3 gives the results obtained for CO_2 permeabilities and CO_2/CH_4 selectivities.

membrane	P_{CO_2} (Barrer)	α_{CO_2/CH_4}
EPDM	81	4.3
EPDM + NaX 35.8 vol%	199±20	9.8±0.1
EPDM + LiX 35.6 vol%	159±5	8.8±0.1
EPDM + KX 35.3 vol%	156±4	8.4±0.1
EPDM + CaX 35.8 vol%	142±4	7.1±0.2
EPDM + BaX 34.9 vol%	105±10	6.1±0.3
EPDM + NaY 37.7 vol%	275±20	10.8±0.3
EPDM + KY 36 vol%	299±20	15±1.0
EPDM + CaY 37.7 vol%	211±6	9.7±0.1
EPDM + CaLSX 35.8 vol%	69±5	4.3±0.1
EPDM + NaLSX 35.8 vol%	82±3	5.4±0.1

Table 3: Gas separation results obtained with various ion exchanged zeolites.

One can see from table 3 that changing the cations does result in variations of the gas separation properties at essentially constant volume fraction of zeolite in the polymer. The best result for the zeolite X is obtained with Na^+ as cation. Replacing Na^+ with Li^+ or K^+ reduces the carbon dioxide permeability and selectivity over methane. When the bivalent cations Ca^{++} and Ba^{++} are incorporated into the zeolite structure, the gas permeation properties of the filled membranes are considerably worse than with the zeolites mentioned above. To a lower extent this is also observed with Na-Ca exchange for zeolites NaY/CaY and NaLSX/CaLSX.

LiX is not as effective in improving permeability and selectivity as NaX. This might be the result of the water of hydration which is more strongly retained in the case of Li^+, as suggested already [10]. Despite a smaller ionic radius, the lithium ion has a larger effective ionic radius than sodium due to the water of hydration. This might decrease the sorption capacity and slow down the diffusion of the gas molecules through the pores and thus lead to somewhat less improved gas separation properties.

The differences observed between Na^+ and K^+ are quite difficult to understand. In the case of zeolite X (Si/Al=1.2), the potassium exchanged zeolite results in a lower CO_2 permeability and selectivity than the sodium exchanged. The opposite effect is observed with zeolite Y (Si/Al=2.6). The latter result might be explained by the less polarizing effect of K^+ than Na^+, which could mean that less water of hydration remains sorbed. The preferential sorption and diffusion of carbon dioxide would then be more effective than in NaY. Nevertheless, the same effect should be observed in the case of zeolite X. The ratio Si/Al however is low in this case, indicating the presence of more cations in the structure. A size effect might become apparent since the ionic radius of potassium is larger than the one of sodium. This size effect would not be observed in the case of zeolite Y because of a much lower amount of cations in the structure.

The effect observed with bivalent cations might have two origins. The first one is that these cations are larger than sodium or lithium so that they might hinder the diffusion of gas molecules through the pores, especially if they are located near the window opening of Faujasite. It is known from literature that the effective pore size of zeolite CaX is narrower than in the case of NaX [13]. The difference observed between CaX and BaX would then be accounted for by the larger ionic radius of Ba^{++}. Furthermore, CaY also seems less effective than NaY, but the effect is not as considerable as with zeolite X. This might be due to the smaller amount of cations that are present in the Y structure.
The second possible cause is that the interaction between the sorbed carbon dioxide molecules and the bivalent cations is stronger (this was shown for zeolites NaX, NaY, CaX and CaY [9]), resulting in a slower diffusion through the pores.

IV.5- Conclusions

The experimental results in this chapter clearly show that the intrinsic properties of the zeolites and mostly its internal porous system are determining factors with respect to the gas separation properties obtained when zeolites are incorporated into a polymer phase. Surface diffusion at the external surface of the zeolite particle as an important mechanism can be excluded, based on the present results and those presented in chapter III.
The pore size of the zeolite cannot be investigated independently since zeolites with different pore sizes have either various porous networks or different chemical compositions.

One-dimensional porous systems do not lead to any significant improvement of the CO_2/CH_4 separation properties of EPDM. Offretite (3D porous structure) results in a large enhancement of the carbon dioxide selectivity and permeability for carbon dioxide (comparable to KY).

The chemical composition of the zeolite also plays an important part. The Si/Al ratio significantly influences the carbon dioxide permeability of the filled membranes in the case of ZSM-5 and Faujasite zeolites. Too many aluminum atoms in the framework results in a drastic decrease of the separation performances of the filled membranes. This can be explained by the large number of cations which hinder the diffusion of the gas molecules.
The nature of the cation also influences the permeation properties. The presence of bivalent cations in the zeolite pores is not as beneficial as monovalent cations for the selectivity and permeability, which might be the result of a larger size and a different location in the framework.

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Appendices to chapter IV

A.1: Zeolite synthesis and modification

Some of the zeolites investigated in this chapter were prepared by ourselves in the laboratory. This appendix gives the experimental procedures and the material properties.

A.1.1- Synthesis of zeolite Theta-1

Gel preparation
15 ml deionized water is used to dissolve 2.2 g of sodium hydroxide (NaOH) and 2 g of sodium aluminate ($NaAlO_2$). After cooling down 62.3 g of triethylenetetramine is slowly added, followed by 84.58 g of Lévilite (CECA S.A., 86.6% SiO_2) and stirring is carried out to obtain a homogeneous dispersion.

Crystallization
The gel is placed in a Teflon vessel which is then placed in a stainless steel autoclave. Stirring is carried out mechanically (300 tr/mn). The temperature is then increased to 160 °C and the crystallization is carried out for 24 hours.

Washing
After a fast cooling step, the dispersion is filtered on a porous glass support and washed until the washing water reaches pH = 9. Then the zeolite is placed in an oven at 80 °C for drying overnight. The last step is calcination at 600 °C for 10 hours with a temperature increase of 1°C per minute.

Result
X-ray spectra indicated a good crystallization of the zeolite (however not 100%). Scanning Electron Microscopy showed clusters of very small particles which size could not be determined by SEM.

A.1.2- Ion exchange

The cations present in the zeolite structure can be exchanged in order to give different sorption properties to these adsorbents. The various experimental conditions used are given in this appendix. The ionic composition of the zeolites is given in table 2 of appendix A.2.

BaX

The experimental procedure to replace the cations present in zeolite 13X (mainly Na^+) with Ba^{++} cations, consists of percolating 2 liters of a solution of 0.1 M of barium chloride (Merck) through a zeolite bed (20 g) on a porous support (porous glass), followed by washing with demineralized water. The zeolite is then dried overnight at 80°C in air, calcined at 300°C during 2 hours and placed in a vacuum oven at room temperature.

LiX

The procedure is adapted from reference [10]. 20 g of zeolite 13X is placed in 4 l of a 0.1 M aqueous solution of LiCl (Merck). The dispersion is warmed up to 60°C under stirring during 15 hours. The zeolite is then filtrated and washed with demineralized water (4 l). The previous operations are repeated a second time. After drying at 80°C, the zeolite is calcined at 300°C and stored in a vacuum oven at room temperature.

KX

20 g of zeolite 13X (NaX) is dispersed in a 0.15 M KCl (Merck) aqueous solution (2 l) during 15 hours. After filtration and washing with demineralized water, this procedure is repeated. After drying at 80°C, the zeolite is calcined at 300°C during 2 hours and placed in a vacuum oven at 30°C.

CaX

30 g of zeolite 13X is placed in 2 liters of a solution containing 15 g/l of $CaCl_2$ (Merck) and the dispersion is stirred at room temperature during 6 hours. After filtration, the zeolite is washed with demineralized water (about 4 l). Then the previous operations are repeated two more times (the exchange time was then fixed to 15 hours). After drying at 80°C, the zeolite is calcined at 300°C during 2 hours and placed in a vacuum oven at 30°C.

CaY

Same experimental procedure as above (CaX) with NaY as starting zeolite.

NaLSX

Same experimental method with CaLSX as starting zeolite and NaCl as salt.

A.2: Structure and chemical composition of the zeolites investigated

This appendix gives more detailed information about the various zeolites investigated in chapter IV, but also in chapters III and V. At first an overview is shown with some basic information about the ratio Si/Al, the pore size, the direction of the pores and the cations present (table 1). Tables 2 and 3 give the chemical composition of the zeolites used in this study.

Name	Chemical structure	T/1000 (Å^3)	Pore size (Å)	Structure	Si/Al	$\rho_{framework}$ (g / cm^3)	$\rho_{crystal}$ (g / cm^3)	H_2O sorption (wt%)
Type A	$\{Na_{12}(Al_{12}Si_{12}O_{48}) \cdot 27H_2O\}_8$	12.9	3.2-4.3	3D	1	1.27	1.48-1.69	23
ZSM-5	$Na_n(Al_nSi_{96-n}O_{192}) \sim 16H_2O$	17.9	5.3*5.6<->5.1*5.5	2D	10-500	1.76	*	4
Silicalite-1	pure silica form of ZSM-5	17.9	5.3*5.6<->5.1*5.5	2D	∞	1.76	1.76	1
Theta-1	$Na_n[Al_nSi_{24-n}O_{48}] \cdot \sim 4H_2O$	19.7	4.4*5.5	1D	>11	1.96	1.97‡	-
Offretite	$(Ca,Mg)_{1.5}K[Al_4Si_{14}O_{36}] \cdot 14\,H_2O$	15.5	6.7<->3.6*4.9	3D	3-4	1.54	1.68	13
Mordenite	$Na_8[Al_8Si_{40}O_{96}] \cdot 24\,H_2O$	17.2	6.5*7.0<->2.6*5.7	2D	5-6	1.71	1.82	14
Faujasite	$(Na_2, Ca, Mg)_{29}[Al_{58}Si_{134}O_{384}] \cdot 240\,H_2O$	12.7	7.4	3D	1.5-3	1.25-1.29	1.25-1.54	26

* depends on the ratio Si/Al
‡ calculated for Si/Al=50
- unknown

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Table 1: Overview of the various zeolite types investigated.

The results given in Table 2 were obtained by chemical analysis.

Denomination	Si/Al	$\rho_{crystal}$ g.cm^{-3}	Na	K	Ca	Ba	Li	Mg
			mole % of total ion concentration					
3A	1	1.69	55.1	44.4	1.4	-	-	-
4A	1	1.52	98.9	0.8	0.3	-	-	-
5A	1	1.48	24.9	1.8	73.3	-	-	-
ZSM-5 15	14.5	1.79	91	4.7	3.1	-	-	1.2
ZSM-5 25	24.7	1.78	96.2	3.2	-	-	-	0.6
ZSM-5 75	85	1.77	96.3	2.1	-	-	-	1.6
silicalite UOP	500	1.76	-	-	-	-	-	-
NaY	2.7	1.42	98.2	1.8	-	-	-	-
NaY 10	9.5	1.31	100	-	-	-	-	-
NaY 20	19.5	1.30	75	25	-	-	-	-
KY	2.6	1.52	3.5	96.5	-	-	-	-
CaY	2.6	1.37	45.3	0.1	54.4	-	-	0.2
NaX	1.2	1.54	92.8	3.7	3.3	-	-	0.2
CaLSX	1	1.54	16.9	6.1	76.8	-	-	0.2
NaLSX	1	1.54	77.5	0.1	22.3	-	-	0.1
CaX	1.2	1.51	9.8	1.0	89.1	-	-	0.1
KX	1.2	1.67	11.0	86.8	2.1	-	-	0.1
LiX	1.2	1.43	31.2	0.6	1.9	-	66.2	0.1
BaX	1.2	1.84	43	3.1	2.9	43	-	0.2
Offretite	4.4	1.68	27.5	54.5	9.8	-	-	8.2
Mordenite	6.7	1.82	99.8	0.1	-	-	-	0.1
Theta-1	48.3	1.97	59.5	-	36.3	-	-	4.2

- the concentration of the element was below the accuracy of the analysis method.
When not taken from literature, the crystal densities were calculated using the ratio Si/Al determined and the major cations found.

Table 2: Chemical analysis results.

The amount of carbon, nitrogen and hydrogen was determined as well by Elemental Analysis (Elemental Analyser Mod.1106, Carlo Erba-Strumentazione). The zeolites were analysed without pre-evacuation, which means that water molecules were present inside the pores. The aim of this experiment is to determine whether all the organic molecules necessary for the synthesis (templating agent) were removed by the calcination procedure used. When no carbon and no nitrogen are present, the hydrogen which is detected can only be due to adsorbed water. This gives in addition some information about the hydrophilic/hydrophobic character of the various zeolites. Table 3 shows the results obtained.

zeolite	C (wt%)	N (wt%)	H (wt%)
5A	0.10±0.02	0	2.32±0.06
silicalite-1 before calcination	0.08±0.04	0.03±0.02	0.24±0.04
silicalite-1 after calcination	0	0	0.05±0.00
ZSM-5 Si/Al=24.7	0	0	0.35±0.01
ZSM-5 Si/Al=14.5	0	0	0.46±0.00
KY	0	0	2.06±0.00
NaY	0	0	2.52±0.09
13X	0	0	2.31±0.06
CaLSX	0	0	2.62±0.05
Theta-1	0.02±0.00	0.08±0.01	0.40±0.01
Mordenite	0	0	1.15±0.00
Offretite before calcination	3.90±0.02	1.14±0.03	1.73±0.01
Offretite calcined 2 hrs at 300°C	2.28±0.15	0.63±0.02	1.34±0.03
Offretite calcined 2hrs at 500°C	0.64±0.01	0	1.34±0.03
Offretite calcined overnight at 500°C	0	0	1.33±0.01

Table 3: Thermal Element Analysis of various zeolites.

V

ADSORBENT FILLED POLYMERIC MEMBRANES FOR GAS SEPARATION

Part 3: On the transport mechanism through zeolite filled gas separation membranes

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Summary

In order to get a better understanding of the transport mechanism of gas molecules through zeolite filled polymeric films, the effects of diffusion (time-lag), temperature and feed pressure were studied with a mixture of CO_2/CH_4. The time-lag effect shows an unexpected behaviour in the case of hydrophilic zeolites, i.e. an increase in permeability and selectivity at the same time. In this case the presence of hydrated cations determines the time necessary to reach steady state conditions for permeation. Silicalite-1 filled membranes show a time dependency typical for a diffusion controlled transport mechanism. Permeation activation energies were also determined for various gases (He, CO_2, Ar, O_2, N_2, CH_4) and zeolite filled EPDM membranes. The activation energies increase with increasing kinetic diameter of the diffusing molecules considered. Temperature also has a large effect on the selectivities of zeolite filled membranes. Finally, the feed pressure was varied in the range of 1 to 9 bars, showing a slight decrease of the permeability and a constant selectivity for both the unfilled and filled membranes.

V.1- Introduction

This chapter is aimed to clarify the transport mechanism of gas molecules through zeolite filled polymeric membranes by investigating the diffusive response (time-lag) for various types of zeolites and the effect of process parameters such as feed pressure and temperature. At first time-lag experiments with pure gases and a mixture of gases are considered. The study of the non-steady state permeation behaviour of the filled membranes exhibits some interesting indications concerning the transport mechanism. Furthermore, the permeation temperature has been investigated, which allows the determination of the activation energies for permeation of various gases in various zeolite filled polymeric membranes. The effect of temperature on the selectivity for various gas mixtures has also been studied. Finally, the influence of the feed pressure has been investigated.

V.2- Non-steady state gas permeation

V.2.1- Experimental

The membranes were placed in a vacuum oven at 30°C for several days. Then they were mounted in the permeation cells and again vacuum was applied.
The pressure increase at the downstream side of the membrane is recorded in time, once the feed gas is brought into contact with the upstream side. The steady state permeability is determined from the linear part of the plot, and an effective diffusion coefficient (D, $cm^2.s^{-1}$) can be calculated as well by extrapolation of the linear part to zero flux, which defines the time-lag θ [1]. From the time-lag θ the diffusion coefficient can be calculated according to $D=L^2/6\theta$ where L is the membrane thickness. In the case of a zeolite containing polymer, the calculated diffusion coefficient is an effective diffusion coefficient of the membrane considered as a "black box".
These experiments were carried out with pure gases (feed pressure: 5.3 bars), and with a mixture of carbon dioxide and methane (25/75 vol% respectively, feed pressure: 5.3 bars) as well. In this case, the permeability and the selectivity were measured as a function of time (see appendix 1 to this thesis for more details about the gas permeation set-up).

V.2.2- Results and discussion

Table 1 shows the results of diffusion of pure CO_2 and CH_4 obtained for unfilled and filled EPDM.

polymer, zeolite (vol%)	D_{CO_2} ($cm^2.s^{-1}$)	D_{CH_4} ($cm^2.s^{-1}$)	D_{CO_2}/D_{CH_4}	α_{CO_2/CH_4}
EPDM	$8.70.10^{-7}$	$5.32.10^{-7}$	1.64	4.30
EPDM, 5A (49)	$5.2.10^{-8}$	$2.13.10^{-7}$	0.25	5.24
EPDM, silicalite-1 (53.3)	$3.4.10^{-8}$	$9.2.10^{-9}$	3.70	13.30

Table 1: Diffusion coefficients obtained by time-lag measurements with pure CO_2 and CH_4 for unfilled and filled EPDM membranes; feed pressure=5.3 bars; T=25°C.

It can be deduced that the incorporation of silicalite-1 and 5A results in a large increase of the time-lag, and consequently, in a large decrease of the effective diffusion coefficient. These results show the same trend as observed by Paul and Kemp in the case of 5A filled silicone rubber membranes [2]. It is remarkable that in the case of zeolite 5A, the diffusion selectivity is reversed in favour of methane in comparison to the pure polymer. This indicates that the establishment of the steady state concentration profile for carbon dioxide across the membrane is slower than it is for methane.
In the case of EPDM filled with silicalite-1, both diffusion coefficients are also

lower than in the case of the pure polymer, but the diffusion selectivity remains in favour of carbon dioxide and is even more than twice as high as the value for pure EPDM. The permeation selectivity is also greatly improved by more than a factor of three.

This type of experiments was also carried out with zeolites like 13X and KY. However, extremely long time-lag values were observed, which could not be measured accurately.

In addition to experiments with pure gases, non-steady state permeation experiments were carried out with a mixture of carbon dioxide and methane (25/75 vol%).

Typical results obtained with the organophilic zeolite silicalite-1 as filler are given in figures 1 and 2.

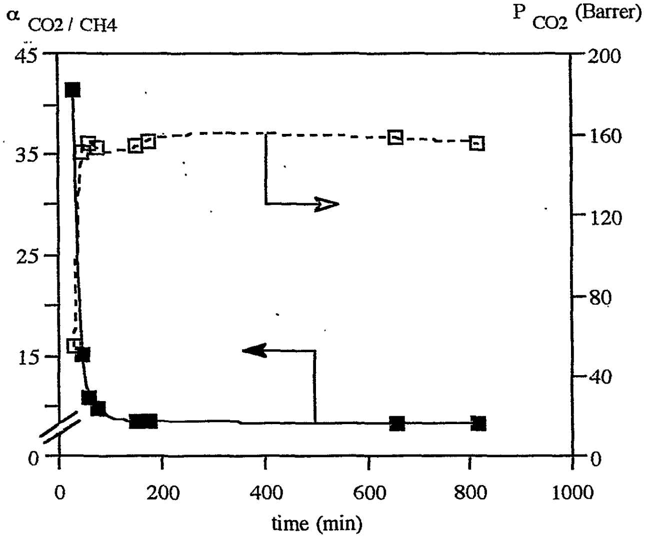

Figure 1: CO_2/CH_4 selectivity and CO_2 permeability versus time for a silicalite-1 filled (32 vol%) EPDM membrane.

The observed behaviour typically corresponds with observations in a glassy polymer membrane. At first, the carbon dioxide molecules diffuse faster than the methane molecules, which means that the carbon dioxide diffusion front arrives first at the permeate side of the membrane, resulting in a very high selectivity. Then, the methane concentration profile is established across the membrane, resulting in a decrease of the selectivity towards the steady state value. This behaviour was observed for various rubbery polymers, both highly permeable (EPDM, figure 1) and poorly permeable (NBR 50, figure 2).

The transport mechanism of gases may be considered as diffusion controlled when silicalite-1 is incorporated into a rubbery polymer. This is clearly indicated by the pure gas time-lag experiments results given in table 1. This statement fits well with the results reported earlier on O_2/N_2 separation [3]. Here the observed improvement could only be explained by a kinetic effect, i.e. the smaller size of the oxygen molecules makes them able to diffuse faster through the silicalite-1 pore system than nitrogen. In the case of CO_2/CH_4, the same phenomenon occurs, coupled with a certain low sorption selectivity of the zeolite for carbon dioxide [4]. This explains why the observed improvement at a given volume fraction for the CO_2/CH_4 separation is larger than for the O_2/N_2 separation.

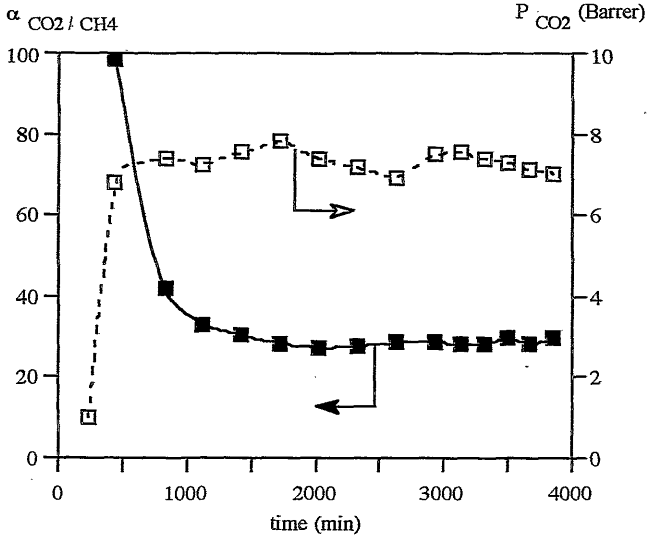

Figure 2: CO_2/CH_4 selectivity and CO_2 permeability versus time for a silicalite-1 filled (50 vol%) NBR 50 membrane.

The same type of experiment carried out with hydrophilic zeolites leads to a totally different and rather unusual time dependency as can be seen in figures 3 to 5.

First a membrane composed of zeolite 5A in EPDM shows an increasing selectivity with time as well as an increasing permeability for carbon dioxide (figure 3). Even more surprising is the fact that the first measurements indicate that the membrane is methane selective, despite a polymeric phase which is selective for carbon dioxide and a zeolite which is also sorption selective for CO_2. The membrane then switches to a carbon dioxide selective behaviour until the intrinsic selectivity of the pure polymer phase and a lower permeability have been reached at steady state conditions.

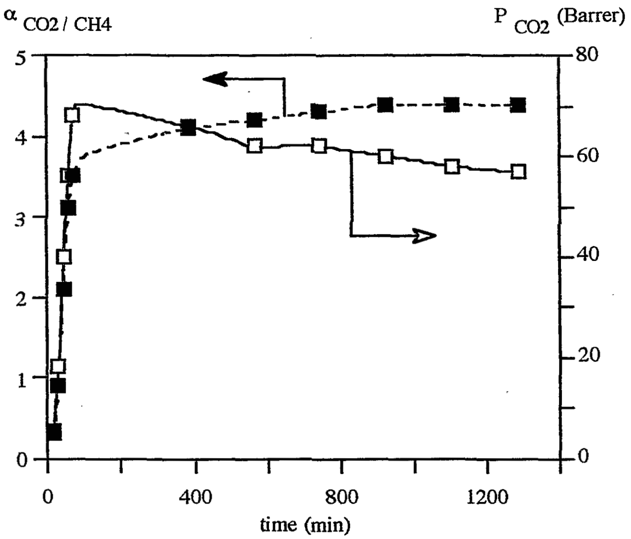

Figure 3: CO_2/CH_4 selectivity and CO_2 permeability versus time for a 5A filled (49 vol%) EPDM membrane.

This dependency on time can be explained by a strong adsorption of the first carbon dioxide molecules diffusing through the membrane into the zeolite porous structure. The zeolite then acts as a trap from which the gas molecules hardly can escape. The hydrophilic zeolite is sorption selective for carbon dioxide, and that is why the methane molecules are trapped to a much lower extent and can diffuse through the polymer phase which results in a methane selective membrane. When the zeolite is in sorption equilibrium with the surrounding polymer phase under permeation conditions, more and more of the CO_2 molecules can diffuse to the permeate side of the membrane, which accounts for the increasing selectivity and permeability. The steady state result indicates that the CO_2 molecules which have been sorbed in the zeolite framework do not participate to the transport mechanism, or to a very small extent, as was already suggested previously [3].

If now a hydrophilic zeolite with a larger pore size is used (13X), the same type of time dependence is observed (figure 4).

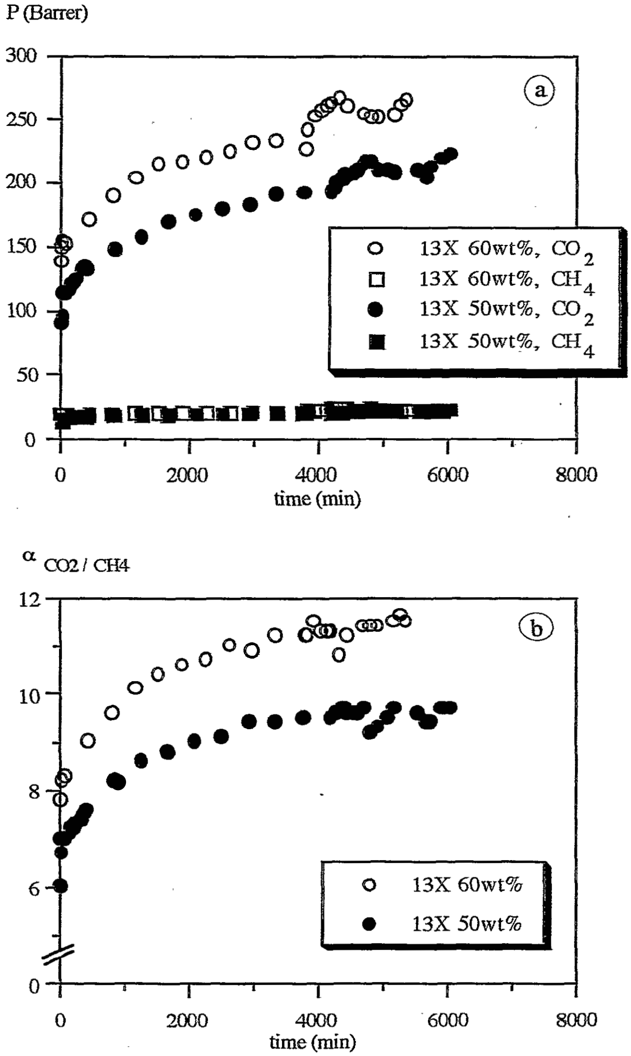

Figure 4: Gas permeabilities (a) and CO_2/CH_4 selectivity (b) versus time of 13X filled EPDM membranes.

One must know that, there is one main difference, i.e. the gas separation properties of EPDM are drastically improved when 13X is incorporated into the polymer matrix.

Here again, both the selectivity and the permeability for carbon dioxide increase with time, but the first measurements indicate a CO_2 selective membrane, with better separation properties than the pure polymer. The steady state permeability and selectivity are reached after a period of 6000 minutes (4 days), which indicates a significantly slower process.

The explanation for the 5A filled EPDM membrane mentioned above also accounts for the results plotted in figure 4. However, in the case of 13X, the sorbed carbon dioxide molecules are not trapped, i.e. they do participate finally to the transport since the selectivity and the permeability are enhanced.

In both cases the transport mechanism may be characterized as pseudo-sorption controlled, in the sense that the sorption of the carbon dioxide molecules into the zeolite pores determines the selectivity and the permeability of the overall membrane in combination with the diffusion of these sorbed molecules from sorption site to sorption site in the zeolite and from the zeolite to the polymer phase.

The question is: what makes this hydrophilic zeolites so special with respect to permeation behaviour ?

The presence of cations in the zeolites 13X and 5A is the main difference if compared to silicalite-1, with exception of the pore size. These cations are normally hydrated. Once incorporated into the polymer phase, these zeolites cannot be totally dehydrated because the polymer cannot withstand the required high temperatures. This means that part of the water of hydration remains in the zeolite pores.

In the case of zeolite 5A this results in a considerable slow down or blocking of the transport of the gas molecules through the pores. This was already reported by Germanus et al. in the case of diffusion of paraffins and olefins in zeolite 13X [5], where a decrease of three orders of magnitude of the diffusion coefficient was observed in the presence of water traces. This was ascribed to the presence of cation-water complexes blocking the cages and the diffusion pathway as well. It was also reported by Wernick et al. [6] that an extremely long time is required to reach steady state of permeation of butane and a methane/isobutane mixture through a single crystal of zeolite NaX. This phenomenon was ascribed to the presence of hydrated cations which hinder the diffusion of gas molecules and have to reorganize themselves in a minimum energy configuration corresponding to the permeation steady state (cation shift). In the case of zeolite crystals incorporated into a polymer matrix, a similar phenomenon is likely to occur. Furthermore, under the applied driving force, some of the hydration water molecules might be gradually removed, making new sorption sites available in the zeolite structure. This means that more and more sites are available for carbon dioxide molecules for sorption and diffusion. A combination of these two effects is most probably responsible for the increase in both permeability and selectivity for carbon dioxide in time.

Experiments carried out with zeolites having basically the same framework as 13X, but a higher Si/Al ratio and consequently less cations, seem to confirm these results. Hence the time dependency of the gas permeation properties of a NaY or KY filled EPDM membrane is less important than for 13X, but still the same trend can be observed. In the case of a dealuminated zeolite Y, almost no time dependence is observed.

Using ZSM-5, a zeolite with a low Si/Al ratio instead of silicalite-1, the steady state selectivity is reached very fast and the permeability increases much more slowly than in the case of a silicalite-1 filled EPDM film (figure 5).

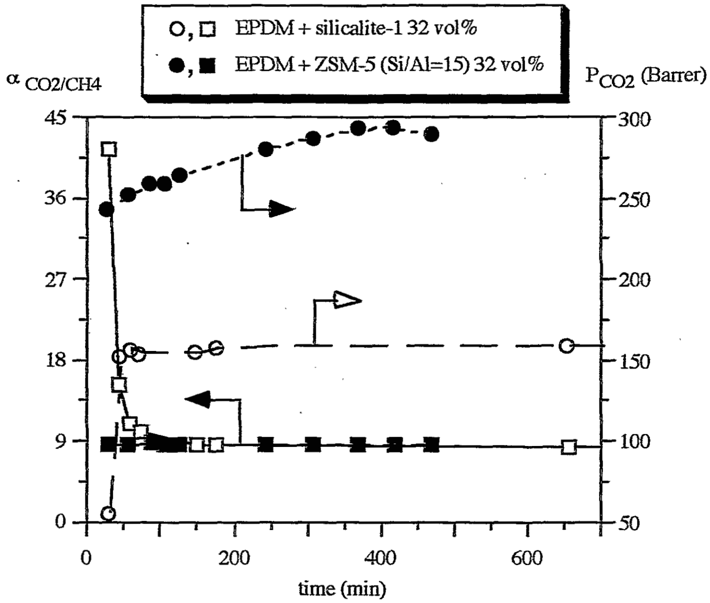

Figure 5: CO_2/CH_4 selectivity and CO_2 permeability versus time for silicalite-1 and ZSM-5 (Si/Al=15) filled EPDM membranes (32 vol% of zeolite).

The slower increase of permeability again can be explained by the presence of cations in the structure. The apparently constant selectivity might be the result of two opposing effects, i.e. a kinetic effect as observed for silicalite-1 and the reordering of the cations as observed in 13X.

This experiment can be compared with the study of Caro et al. who showed that in the case of zeolite ZSM-5, the mobility of water molecules decreases with increasing amount of aluminum in the framework [7]. This was not observed for a less strongly interacting molecule like methane [8].
All these results suggest that the typical permeation behaviour of zeolites 5A, 13X and to a lower extent NaY and KY when incorporated into a polymer phase is indeed affected by the presence of the hydrated cations.

V.3- Temperature effect

V.3.1 - Principle

One may describe the permeation of gas molecules through a membrane as an activated process and define a permeation activation energy E_p ($kJ.mol^{-1}$). The permeability is then dependent on temperature according to the equation:

$$P = P_0 \exp(-E_p / RT)$$

A plot of ln (P) versus 1/T should then give a straight line from which E_p can be determined from the slope of the line.

The activation energy for permeation E_p may be subdivided into an activation energy for sorption (E_s) and an activation energy for diffusion (E_d). Based on the well-known relation P = D * S, one can write:

$$P = D_0 \exp(-E_d / RT) * S_0 \exp(-E_s / RT)$$

and $$E_p = E_d + E_s$$

E_s is the heat of solution in the case of a pure polymer phase, and the heat of sorption in the case of an adsorbent.

V.3.2- Experimental

The experiments were carried out with a double-walled cell. The temperature was varied in the range of 0 to 30°C with incremental steps of 5°C.

The permeability was measured as described previously (see appendix 1 to this thesis). Carbon dioxide, methane, oxygen, nitrogen, helium and argon were used as gases, all at a feed pressure of 5.3 bars. Figure 6 shows a very good linear relationship of ln(P/l) versus 1/T for EPDM filled with 32 vol% of silicalite-1. This indicates that the gas permeation through this membrane is indeed an activated process. Other rubbery membranes have been used as well.

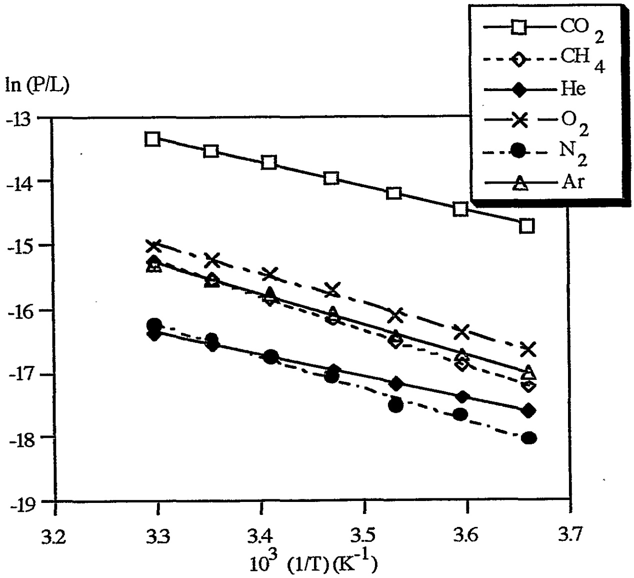

Figure 6: Determination of the activation energies of permeation of various gases through a silicalite-1 filled EPDM film (32 vol% of zeolite).

Furthermore these experiments allow to investigate the effect of temperature on the membrane selectivity for various pairs of gases.

V.3.3- Results and discussion

The activation energy of nitrogen in a silicone rubber membrane as calculated from the ln(P/l) versus 1/T plot is $E_p = 10.55\ kJ.mol^{-1}$, which is in good agreement with literature values ($E_p = 10.78\ kJ.mol^{-1}$ [9]).

Table 2 gives the activation energies obtained with four different EPDM membranes and six gases; also included are literature data of two other polymer membranes [10].

membrane	permeation activation energy E_p (kJ.mol^{-1})					
	CO_2	CH_4	O_2	N_2	He	Ar
EPDM (Keltan 578)	38.6±0.8	47.9±3	44.5±1	46.7±1	35.8±1	46.2±1
Poly(ethylene-co-propylene) [10]	-	-	-	43.8	27.6	39.6
Polyethylene (LDPE) [10]	38.9	47.3	42.7	49.4	34.8	45.2
EPDM + silicalite-1 32 vol%	32.2±2	45.5±4	38.4±3	43.4±2	29.6±3	40.9±3
EPDM + KY 36 vol%	28.1±1	40.4±2	31.8±1	38.2±2	24±2	35±2
EPDM + 13X 36 vol%	32.4±1	43.8±1	36.8±1	41.5±3	27.7±2	41.7±2

Table 2: Experimental activation energies for permeation of various gases in zeolite filled EPDM membranes (feed pressure=5.3 bars) and literature data for related polymers [10].

The values obtained for pure EPDM agree well with literature values for related polymer materials. It is now possible to plot the permeation activation energies of the various gases through the different membranes as a function of the kinetic diameter of the gas molecules. The kinetic diameter given in table 3 is defined as the intermolecular distance of closest approach for two molecules colliding with zero initial kinetic energy [11]. Figure 7 shows the result.

gas	He	CO_2	Ar	O_2	N_2	CH_4
kinetic diameter (Å)	2.60	3.30	3.40	3.46	3.64	3.80

Table 3: Kinetic diameters of the various gases investigated [11].

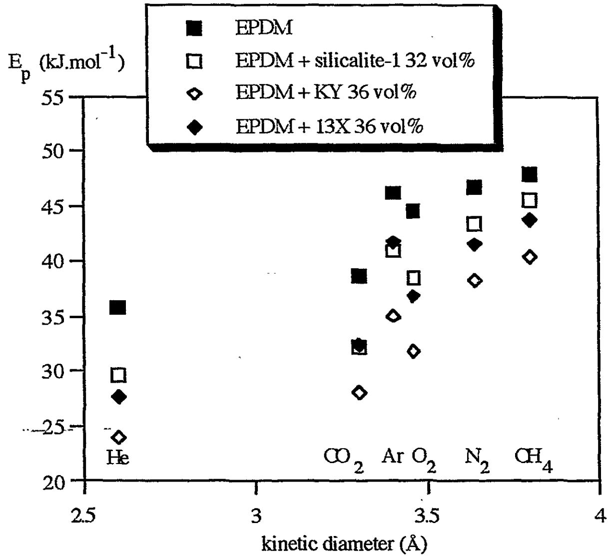

Figure 7: Permeation activation energies of various gases versus their kinetic diameter for pure and filled EPDM membranes.

It can be seen that the larger the kinetic diameter, the higher the permeation activation energy. In addition, the zeolite filled EPDM membranes show a lower E_p value than the pure polymer phase, which means that for all the gas molecules considered, the transport is facilitated.

One might then define a facilitation factor as:

$$\text{facilitation factor} = (E_p^{\,p} - E_p^{\,z+p}) / E_p^{\,p}$$

with $E_p^{\,p}$: activation energy of permeation of the unfilled membrane
$E_p^{\,z+p}$: activation energy of permeation of the filled membrane

A facilitation factor equal to zero means that the zeolite has no effect on the activated permeation of molecules through the overall membrane. When it is positive, the zeolite facilitates the transport of the gas molecules. When it is negative, the activated permeation of the molecules is hindered by the presence of the zeolite. One may then compare it with a molecular sieving effect.

Figure 8 shows the facilitation factor versus the kinetic diameter of the gases investigated.

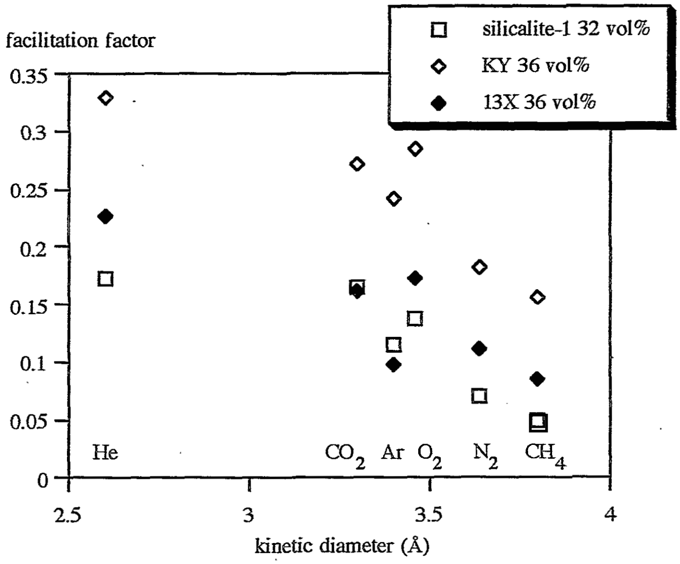

Figure 8: Facilitation factor $((E_p^p - E_p^{z+p})/E_p^p)$ versus the kinetic diameter of the gas molecules for filled EPDM membranes.

As expected from figure 7, the transport is facilitated for all gases and the facilitation factor decreases with increasing kinetic diameter of the gas molecules. No molecular sieving is observed in the range of molecular dimensions investigated; this may be expected for molecules with a kinetic diameter larger than 4.0 Å as can be deduced from figure 8.

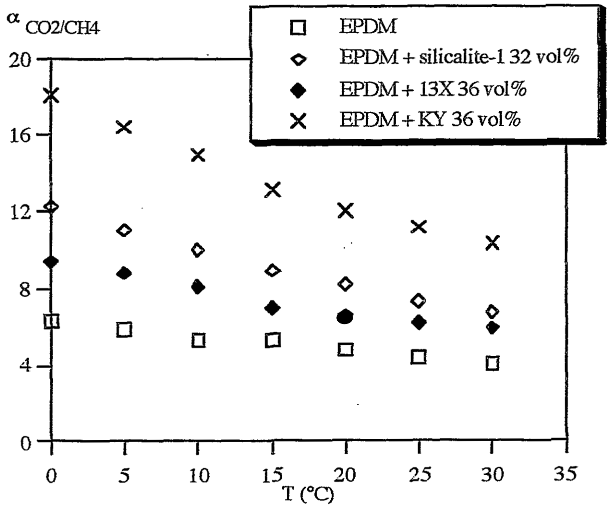

Figure 9: CO_2/CH_4 selectivity versus temperature for unfilled and filled EPDM membranes.

Not only the activation energies for permeation, but also the dependence of selectivities on temperature is interesting. Figures 9 to 11 show variations which are typical of the selectivity for various pairs of gases and membranes.

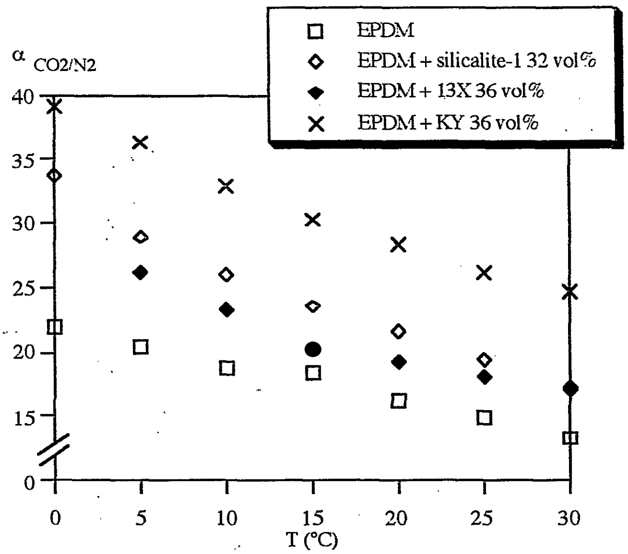

Figure 10: CO_2/N_2 selectivity versus temperature for unfilled and filled EPDM membranes.

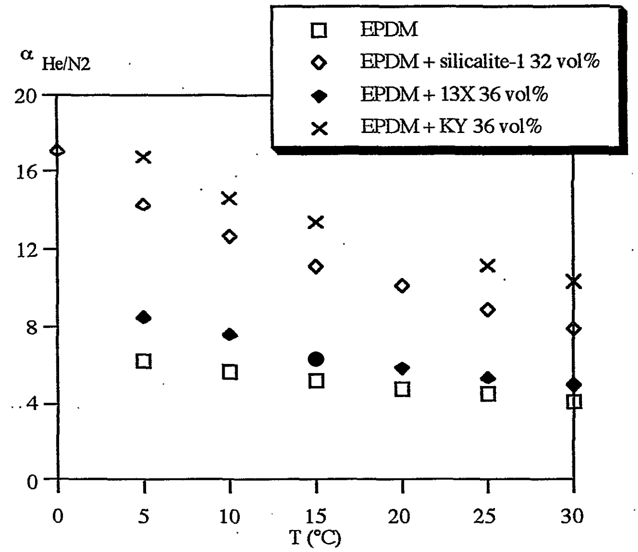

Figure 11: He/N_2 selectivity versus temperature for unfilled and filled EPDM membranes.

One can see that selectivities for the filled membranes are always higher than that of the unfilled polymer over the full temperature range and that the incorporation of zeolites in EPDM makes the material more dependent on temperature with respect to selectivity. For example, in the case of CO_2/CH_4

separation, the selectivity of pure EPDM varies in the range 4 at 30°C to 6.5 at 0°C. When filled with 32 vol% of silicalite-1, the selectivity is in the range 7 to 12 and when filled with 36 vol% of zeolite KY the selectivity varies between 11 and 18.

It may be noticed that fairly high selectivities for carbon dioxide over nitrogen are obtained in the case of KY and silicalite-1 filled EPDM membranes. At 25°C, the selectivity of the KY filled membrane is about 26 with a carbon dioxide permeability of 300 Barrer.

V.4- Pressure effect

The feed pressure might also be of importance for the separation properties of zeolite filled membranes. Experiments were conducted to study this effect.

V.4.1- Experimental

The same gas separation set-up as usual was employed, with a feed mixture of carbon dioxide and methane (25/75 vol% respectively). The feed pressure could be varied in the range 1 to 9 bar. The permeate pressure was kept below 0.1 mbar.

V.4.2- Results and discussion

Figure 12 shows the effect of the total feed pressure on the permeability of unfilled and silicalite-1 filled EPDM films (32 vol%) for carbon dioxide and methane.

In both filled and unfilled membranes a decrease of the permeability with increasing upstream pressure can be observed. This phenomenon is somewhat more pronounced in the case of filled membranes.

Figure 13 shows that the selectivity remains essentially constant over the pressure range investigated.

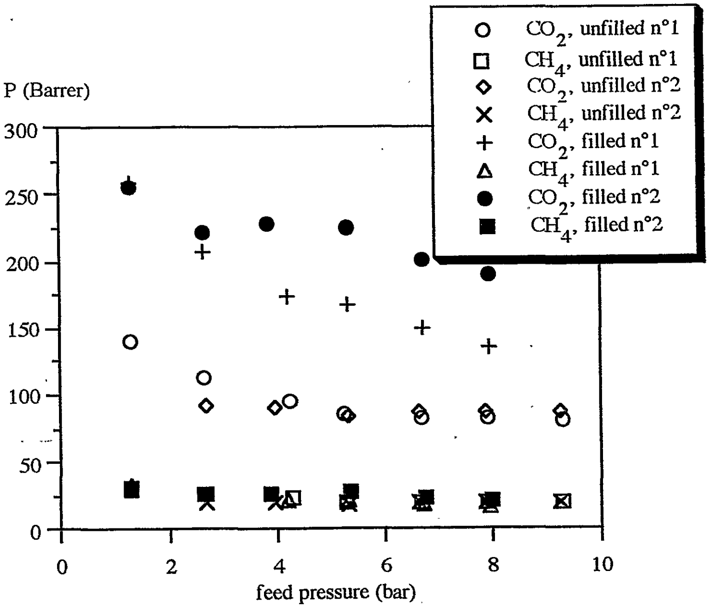

Figure 12: Effect of the total feed pressure on the gas permeability of unfilled and silicalite-1 filled (32 vol%) EPDM membranes; feed mixture CO_2/CH_4 (25/75 vol%).

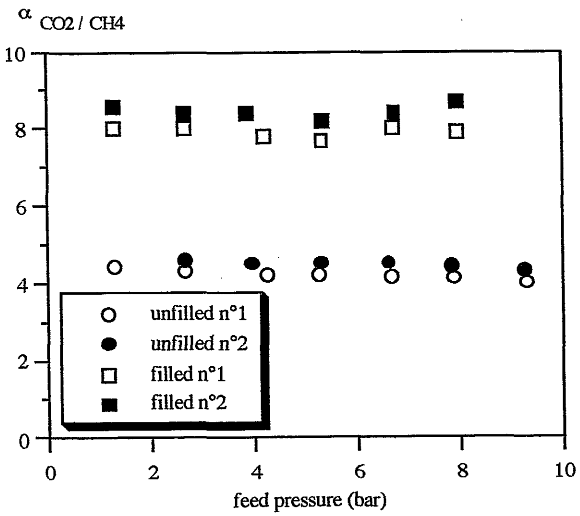

Figure 13: Influence of the feed pressure on the CO_2/CH_4 selectivity of unfilled and silicalite-1 filled (32 vol%) EPDM films; feed mixture CO_2/CH_4 (25/75 vol%).

For the filled membranes, the effect of the zeolite on permeability is larger at lower pressures, due to a relatively large contribution of the zeolite to the overall sorption in the membrane too. At a higher pressure, the sorption by the zeolite does not increase much, but the sorption in the polymer phase does

increase proportionally.
Another explanation may be a compaction effect, i.e. the polymer chains become more and more close packed under increasing feed pressure, resulting in a lower permeability. This is corroborated by a slight decrease of the permeability of the pure polymer membranes.

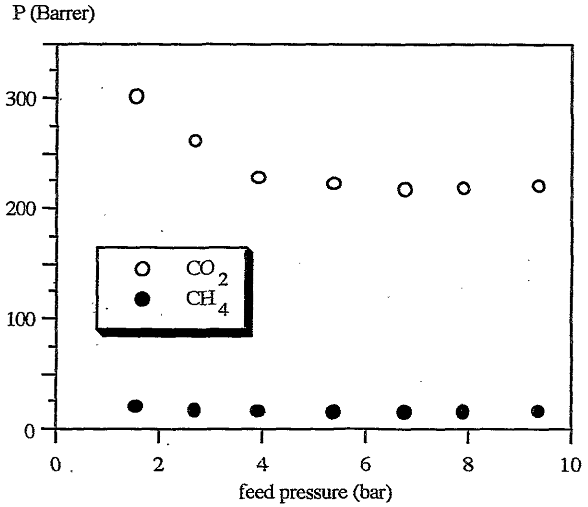

Figure 14: Effect of the feed pressure on the gas permeability of a silicalite-1 filled (53 vol%) EPDM membrane; feed mixture CO_2/CH_4 (25/75 vol%).

Figure 14 shows the same behaviour as figure 12, but for a larger volume fraction of silicalite-1 in EPDM.

Figures 15 and 16 show the kinetics of the pressure effect, i.e. the effect in time following a change in feed pressure with respect to permeability and selectivity.

For these experiments the membrane was first mounted in the cell and the feed brought into contact at initial time at the pressure indicated (1.5 bars). One can recognize at this applied pressure the typical time dependency as reported in a previous section which is characteristic for the silicalite-1/EPDM system (decrease of selectivity and increase of permeability with time until steady state is reached). Upon increasing the feed pressure stepwise, the same kinetic phenomenon is observed to an extent which decreases when the applied feed pressure becomes larger.

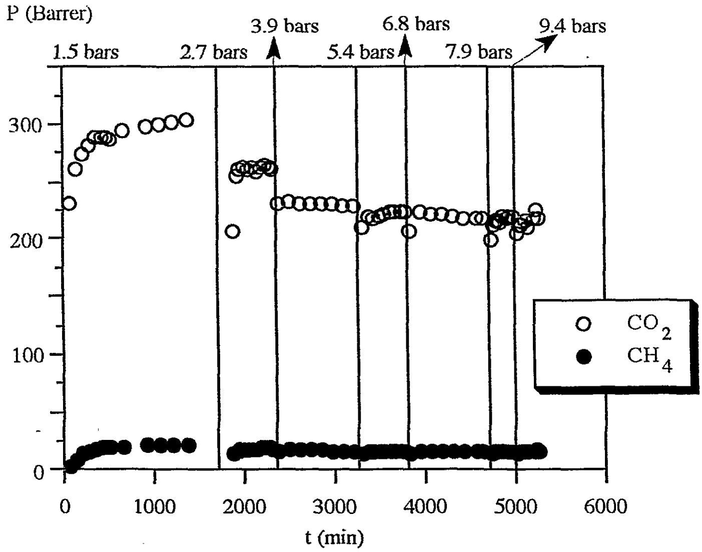

Figure 15: Gas permeability versus time for a silicalite-1 filled (53 vol%) EPDM film at a stepwise increasing feed pressures; feed mixture CO_2/CH_4 (25/75 vol%).

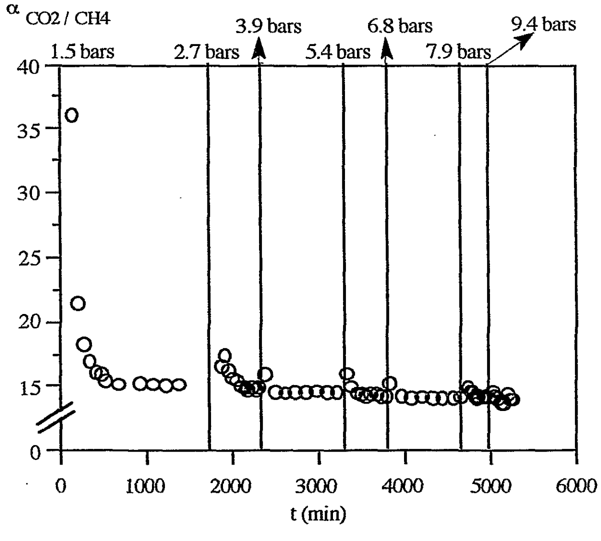

Figure 16: CO_2/CH_4 selectivity versus time for a silicalite-1 filled (53 vol%) EPDM film at stepwise increasing feed pressures; feed mixture CO_2/CH_4 (25/75 vol%).

It may be argued that this is again a confirmation of the diffusion controlled mechanism in this type of membranes. In addition, the decreasing impact of pressure steps on the gas separation properties both in time and at steady state means that at these pressures, the permeation in the zeolite particles is not really influenced any more.

V.5- Conclusions

Non-steady state permeation experiments with a CO_2/CH_4 mixture allow to distinguish two types of behaviour for zeolite filled membranes. Polymer films containing the organophilic zeolite silicalite-1 show a typically diffusion controlled transport of gas molecules which can be compared with observations for glassy polymer membranes, i.e. a fast decrease of the selectivity with time and a fast increase of the permeability towards steady state.

Hydrophilic zeolites (5A, 13X) result in a totally different behaviour, i.e. an increase of both selectivity and permeability with time. This phenomenon is explained by the presence of hydrated cations in the zeolite structure which hinder the sorption and the diffusion of guest molecules. The transport mechanism is so-called pseudo-sorption controlled.

The temperature dependency of gas permeabilities through zeolite filled membranes shows that the permeation is an activated process. The permeation activation energies increase with the kinetic diameter of the permeating molecule. No molecular sieving effect is observed with the gases investigated. Finally, the applied feed pressure has no effect on the selectivity in the range investigated (1 to 9 bars) and results in a slight decrease of the permeability.

Acknowledgments: The authors wish to thank L.Philippi for measuring the effect of temperature on the permeation properties.

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VI

ADSORBENT FILLED POLYMERIC MEMBRANES FOR GAS SEPARATION

Part 4: Zeolite transport properties

Summary

In the previous chapters of this thesis the positive effect of certain zeolites on the gas separation properties of rubbery polymers was demonstrated. The gas permeation and sorption results can be modelled by various methods which may results in a better understanding of the transport phenomena in these zeolite filled membranes. For this purpose, permeability models are used to describe the system silicalite-1/EPDM in the case of the CO_2/CH_4 separation. In this way a "zeolite permeability" is obtained of which the significance is discussed here. The dual mode sorption approach is used to model the equilibrium gas sorption isotherms as well as the transient state sorption phenomena. Activation energies of permeation of the filled membranes can also be modelled, resulting in an activation energy of permeation in the zeolite. Finally, a separation power is defined which enables to compare various zeolites with respect to their effect on the permeability and selectivity of rubbery polymers.

VI.1- Introduction

The incorporation of fillers of various kinds in polymer matrices has been studied for many years. The first aim was the improvement of the mechanical properties of the polymer material. Apart from that, the effect of fillers on the transport properties of polymer matrices has also been investigated [1-4]. Most of this early work did not account for any contribution of the filler itself to the transport through the polymer films and only tortuosity effects were considered.

In the previous chapters of this thesis it was shown that in some cases, one only can account for the experimental results if a transport of the diffusing molecules through the channel network of the zeolite particles occured. Various theories and models may be used to describe the transport through these materials. In this chapter, some of these concepts are considered to model the previously reported experimental results.

At first permeability models developed for the diffusion and permeation of species through heterogeneous media have been investigated. Secondly, the dual mode sorption approach is applied to model equilibrium and kinetics of sorption in zeolite filled membranes. Finally an activation energy of permeation through silicalite-1 is calculated from the activation energies determined for the filled membranes and a permeability model.

VI.2- Permeability models

VI.2.1- Background

In chapter II of this thesis, the pervaporation of a toluene/ethanol mixture by means of active carbon filled membranes was described by the model developed by te Hennepe [9]. Various other models can be found in literature which aim to describe the permeability in heterogeneous (composite) systems [5-10]. A polymer membrane containing adsorbent particles is a typical example of such a heterogeneous medium. One of the most simple ways of describing the permeability in these systems is a geometrical mean relation [8], as expressed in equation (1):

$$\ln (P) = \phi_z \ln (P_z) + (1-\phi_z) \ln(P_r) \qquad (1)$$

where
P : permeability through the composite medium (Barrer)
P_z : zeolite permeability (Barrer)
P_r : polymer permeability (Barrer)
ϕ_z : zeolite volume fraction in the composite membrane (-)

This equation has been used for instance to model the permeability of a copolycarbonate as a function of the amount of bisphenol A, showing a good agreement of the measured permeability with the calculated one [11].

The model developed by te Hennepe for pervaporation [9,10] can be adapted to gas separation. It is based on a resistance model including geometrical considerations adapted from Nielsen [5]. The equation derived for pervaporation with active carbon filled polymeric membranes has been given in chapter II of this thesis.

This equation can easily be modified to express the permeability of a component through a zeolite filled membrane as a function of the volume fraction of zeolite:

$$P_i = \frac{1}{\dfrac{(1-\phi_z^{1/3})}{P_{r,i}} + \dfrac{3/2\,\phi_z^{1/3}}{P_{r,i}(1-\phi_z) + 3/2\,\phi_z P_{z,i}}} \qquad (2)$$

in which:
P_i : permeability of component i (Barrer)
$P_{r,i}$: pure polymer permeability of component i (Barrer)
$P_{z,i}$: zeolite permeability of component i (Barrer)
ϕ_z : volume fraction of zeolite in the membrane (-)

This model was derived assuming that the polymer and the zeolite permeabilities are independent of the zeolite content in the membrane and that the particles are cubic, which is a good approximation in the case of silicalite-1. Furthermore any variation of the zeolite permeability due to its location in the membrane (feed or permeate side) is not taken into account. Both permeabilities are average values over the whole membrane thickness. A more complete and critical discussion of this model is given in the appendix to this chapter.

Petropoulos [8] reviewed the various approaches found in literature to describe the permeability of binary composite materials. Among the various models described, the one originally developed by Maxwell seems also suitable for the system investigated here. The final equation is:

$$\frac{P_i}{P_{r,i}} = 1 + 3\phi_z\left[\frac{\alpha+2}{\alpha-1} - \phi_z\right]^{-1} \quad ; \quad \alpha = \frac{P_{z,i}}{P_{r,i}} \tag{3}$$

with:

P_i : permeability of the composite film (Barrer)
$P_{r,i}$: permeability of the pure polymer (Barrer)
$P_{z,i}$: permeability of the zeolite (Barrer)
ϕ_z : zeolite volume fraction in the film (-)

Equation 3 was originally derived for "a dilute dispersion of spheres, in which interparticulate distances are sufficiently large to ensure that the flow line pattern around any one sphere is practically undisturbed by the presence of the others". However, Petropoulos showed that this equation appears to be valid over the whole concentration range of composition for an isotropic dispersion of isometric particles of proper shape and mode of packing, ensuring that the particles in question are well-separated from one another.

An assumption which is common to all these models is that the film only consists of two phases. This means that the presence of filler particles does not influence the properties of the polymer phase in the surrounding of a particle. This would create a third phase which may consist of microvoids as described by Barrer [6]. In chapter III, it is shown that at very large volume fractions of adsorbent in the polymer phase, voids are created which drastically increase the permeability of the membrane. The experimental data which clearly showed the occurence of microvoids were not considered here in the modelling procedure.

Furthermore, these model equations assume that the two dictinct domains are non-interacting, that their permeabilities are independent of each other and that in the composite medium they are not much different from what can be measured for the pure materials.

VI.2.2- Results and discussion

The permeability models described in the previous paragraph are first applied to the case of an impermeable filler. The system silicone rubber/silica has been investigated with oxygen and nitrogen as permeants. In this case, the adsorbent permeability is fixed to zero (impermeable filler) and equations (2) and (3) are applied. Actually no model fitting is carried out here, but just a comparison of the model prediction to the experimental data is given. Figure 1 shows the result.

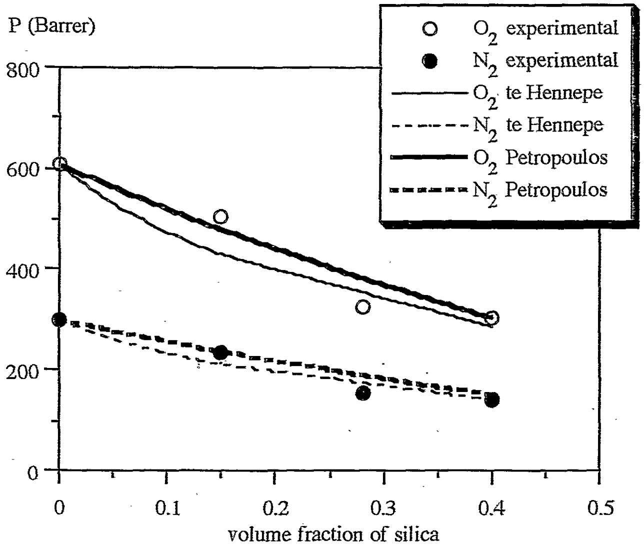

Figure 1: Application of the models of te Hennepe [9] and Petropoulos [8] to silicone rubber filled with non-porous silica; oxygen and nitrogen as permeants; feed pressure 5.3 bars.

One can see that the fit between the two models and the experimental data is quite good in the case of a non-permeable filler. This also means that no surface diffusion at the external surface of the solid particles takes place.

The second investigated system is EPDM + silicalite-1 using CO_2/CH_4 as gas mixture.

One could assume that instead of a porous filler with pores of fixed size, the composite membrane consists simply of voids in the micrometer range surrounded by the polymer phase. The permeability of these voids is extremely large compared with that of the polymer, and essentially equal for all gases (diffusion in the gas phase). Figure 2 shows the model prediction (Petropoulos, eq.(3)) for the selectivity in the case of the gas mixture carbon dioxide/methane and EPDM as polymer. The permeability in the voids is arbitrarily fixed at 10^5 times the CO_2 permeability of EPDM and is the same for CO_2 and CH_4.

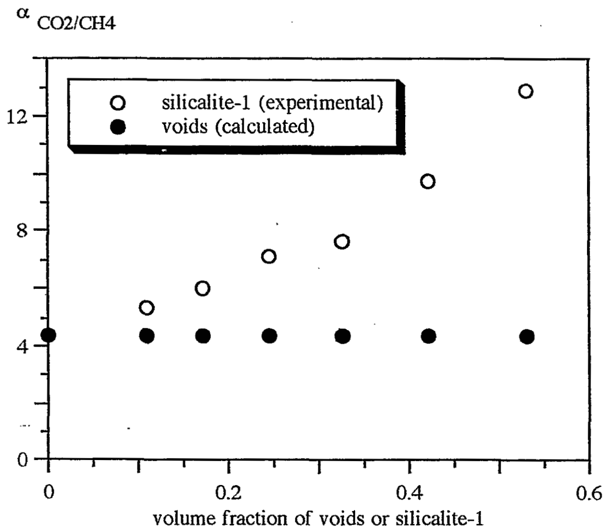

Figure 2: CO_2 selectivity of EPDM filled with silicalite-1 (experimental) or with voids (calculated) versus volume fraction of "filler"; the points representing the voids are obtained by means of Petropoulos' model (equation (3)).

This figure shows that simply the presence of voids would not result in an increase in selectivity. This means that the transport properties of the zeolite itself are responsible for the selectivity increase of the composite membranes compared to the unfilled polymer.

In the case of EPDM filled with silicalite-1, the three models are fitted in figure 3 to the data given in chapter III, i.e. the gas permeability of the silicalite-1 filled membranes versus the volume fraction of zeolite in the films. Here, the model only uses one fitting parameter which is defined as the "zeolite permeability" (expressed in Barrer). The rubber permeability is obtained from the experiment with the unfilled polymer. Figure 3 shows the results obtained with the three models.

It can be seen that all the models fit very well to the experimental data. The fit is much better than what was obtained by te Hennepe for the system silicone rubber/silicalite-1 used in the pervaporation of alcohol/water mixtures [9]. Furthermore, the three models do not differ much as can be seen from figure 3.

Figure 4 shows the experimental and modelled selectivity as a function of volume fraction of silicalite-1 in EPDM. Here again, the fit is satisfactory and a little better for Petropoulos' and the geometrical mean model than for te Hennepe's model.

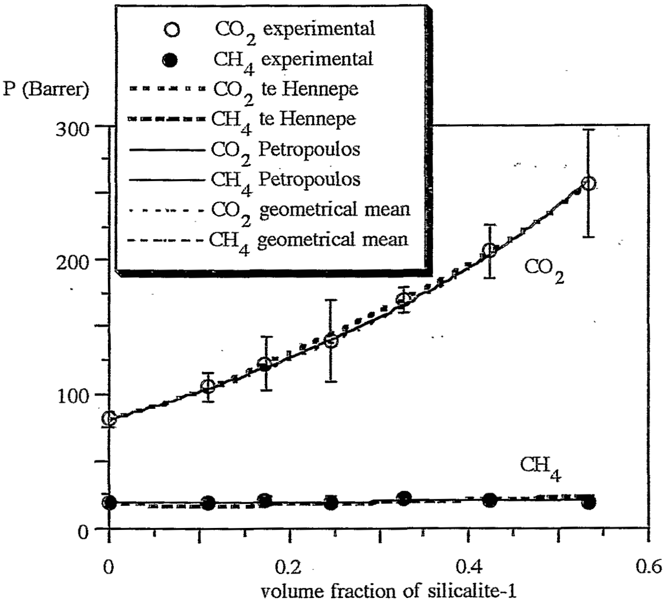

Figure 3: Experimental and modelled gas permeabilities of silicalite-1 filled EPDM films versus volume fraction of silicalite-1.

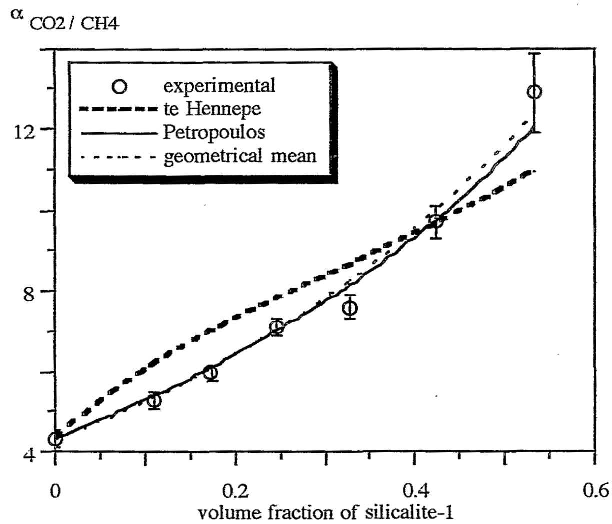

Figure 4: Experimental and modelled selectivity for CO_2 in the case of the EPDM/silicalite-1 system.

Table 1 gives the fitting parameters obtained from the two models considered.

model	P_{z,CO_2} (Barrer)	P_{z,CH_4} (Barrer)	α_{CO_2/CH_4}
geometrical mean, eq.(1)	713	23	31.3
te Hennepe, eq. (2)	919	35	26.3
Petropoulos, eq. (3)	1020	24	42.5

Table 1: Silicalite-1 "permeabilities" and selectivities for CO_2/CH_4 obtained from various permeability models; silicalite-1 is embedded in EPDM.

As can be expected from figures 3 and 4, the three models result in comparable zeolite permeabilities and selectivities. Undoubtedly these values tend to describe silicalite-1 as a very interesting material to be used for gas separation, since a large permeability and a reasonable selectivity are obtained from the models. This might be the case, but experimental results obtained with pure zeolite membranes are not yet available to confirm these values (see chapter I). However, the physical significance of these zeolite permeabilities can be controlled indirectly. For this purpose, the carbon dioxide permeability of membranes containing silicalite-1 prepared with other polymer materials was calculated using the fitting parameters P_{z,CO_2} and P_{z,CH_4} obtained from the system EPDM/silicalite-1. These calculated permeabilities are compared with the experimentally measured values and the results are given in table 2.

membrane	$P_{CO_2, exp.}$	$P_{CO_2 \text{ te Hennepe}}$	$P_{CO_2 \text{ Petropoulos}}$
NBR50 + silicalite-1 50 vol%	7.2	15.6	13.0
NBR45 + silicalite-1 50 vol%	14	25.5	21.5
Polychloroprene + silicalite-1 50 vol%	22	56.9	49.2
PDMS + silicalite-1 46 vol%	6200	1662	1950

Table 2: Comparison of experimentally measured CO_2 permeabilities to model predictions using the zeolite permeability determined from the system EPDM/silicalite-1; the CO_2 permeabilities are expressed in Barrer.

One can see that the zeolite permeability determined from the EPDM/silicalite-1 system cannot predict the permeability results for other silicalite-1 filled polymers. The model predictions obtained from the geometrical mean relation (not given in the table) are even worse than the two presented here. It can be concluded that the zeolite permeabilities obtained from the models are system specific and for this case characteristic of the system EPDM/silicalite-1 used for the CO_2/CH_4 separation. They are not intrinsic properties of silicalite-1 and thus they cannot be considered as a pure material characteristic representing the separation properties of a pure silicalite-1 membrane. A reliable way to obtain the real zeolite permeability is to perform measurements directly through a single silicalite-1 crystal or a pure silicalite-1 membrane, provided the permeation only occurs through the micropores and not through cracks or other imperfections (see chapter I).

The results indicate that the polymer phase surrounding the zeolite particles does influence the transport properties of the zeolite itself, which is in contradiction to the assumptions mentioned previously. The less permeable the polymer is, the lower the zeolite permeability calculated by the permeability models (see figure 5). The line going through the points is just to guide the eye. The ratio of the zeolite permeability to the polymer permeability is in the range 3 to 8 depending on the polymer considered.

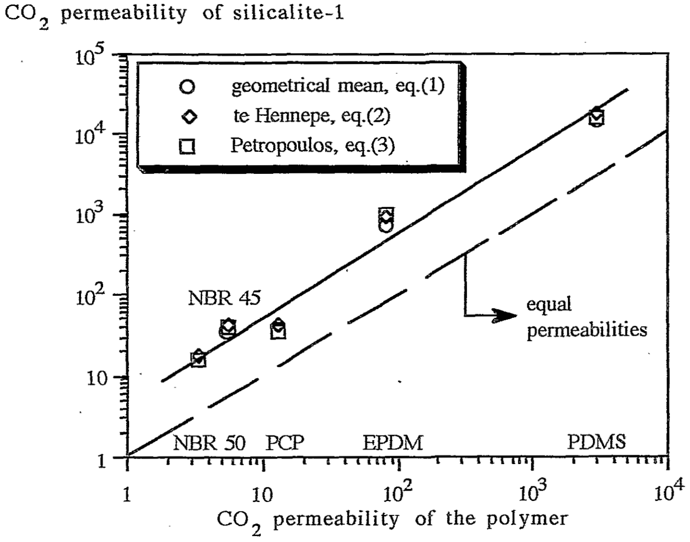

Figure 5: CO_2 permeability of silicalite-1 (obtained from the three models) versus permeability of the polymer phase.

This means that the transport phenomena at the interface polymer-zeolite pore are important. The steps, desorption from the polymer and sorption into the zeolite, and, desorption from the zeolite and sorption into the polymer, must be involved in the transport mechanism. In the case of an equilibrium sorption experiment, the number of molecules sorbed into the zeolite is independent of the polymer phase present around the particles. It is only a function of the partial pressure (or fugacity) of the CO_2 molecules in the surrounding gas phase. Only the kinetics of sorption may differ from one polymer to the other, but the final equilibrium sorption in the zeolite particles remains the same. On the other hand, in the case of permeation which is a non-equilibrium process, both sorption and diffusion contribute to the permeability. The number of molecules effectively diffusing into and out of a zeolite particle depends on the local activity difference of the gas molecules in the polymer phase around this particle. The activity (or fugacity) of the gas molecules in the polymer phase depends on the concentration and the interaction with the polymer chains. The activity profile in the polymer phase varies from one polymer to the other under the same permeation conditions, due to different sorption values and sorption-desorption rates. For example the solubility coefficient of carbon dioxide in EPDM at 30°C is 0.783 $cm^3STP.g^{-1}.bar^{-1}$, whereas in PDMS at 35 °C it is only 0.127 $cm^3STP.g^{-1}.bar^{-1}$ (see next section and reference [12]). This means that the concentration or activity profile in the polymer phase accross the membrane is steeper in the case of EPDM than in the case of PDMS and consequently for two membranes of equal thickness, a zeolite particle situated at the same distance from the permeate side is in a steeper gradient of carbon dioxide concentration in the case of EPDM than in the case of PDMS. The models lead to a mean value of the zeolite permeability, independent of the place in the membrane, but this mean value does not correspond to the same activity gradient.

A molecule diffusing into a zeolite particle has first to desorb from the polymer and this is strongly dependent on the polymer itself. For example the heat of solution of carbon dioxide in Low Density Polyethylene is 0.4 kJ/mol, in polychloroprene -9.6 kJ/mol and in a Nitrile Butadiene Rubber containing 27% of acrylonitrile segments -10.9 kJ/mol [13]. When a molecule diffuses out of the zeolite particle, it has to sorb again in the polymer phase, which means that globally, the energy balance at the external surface of the particle is zero. However, the sorption-desorption step could introduce an additional resistance to transport at the interface polymer/zeolite.

A surface barrier effect could indeed be a cause of the large discrepancy in zeolite permeabilities. This surface barrier would be larger for poorly permeable polymers (low diffusion coefficient) and result in low zeolite permeabilities. This actually means that an interfacial resistance exists, where the transfer from the polymer to the zeolite is controlled by the polymer permeation properties. It can be compared with a concentration polarization effect, as observed for the removal of trace organics from water by pervaporation [14]. In this case, a boundary layer in the liquid phase is present which introduces an extra resistance for the transport of the organic molecules. In the case of a zeolite particle embedded in a polymer, the zeolite permeability is much larger than the polymer permeability so that such a interfacial layer might be created and thus an external resistance at the interface polymer/zeolite introduced. This resistance is polymer dependent and becomes larger when the polymer permeability decreases and thus the zeolite permeabilities obtained from the models decrease (see figure 5). The permeability models actually account for the two resistances (in the interfacial layer and in the zeolite) since they assume the two phases to be independent.

VI.3- Dual mode sorption approach

Carbon dioxide sorption isotherms for pure and zeolite filled EPDM membranes have been given in chapter III of this dissertation. It was shown that the sorption capacity of the membrane is drastically enhanced by the incorporation of zeolites. Furthermore, the polymer itself obeys a Henry's type of sorption behaviour whereas the filled polymer behaves typically like a glassy polymer material. The sorption in glassy polymers is often described by the dual mode sorption model.

VI.3.1- Theoretical background

The dual mode sorption theory was originally suggested by Meares [15]. It has been extensively applied to the description of sorption and permeation of gases through glassy polymer membranes [16-19] but also in the case of adsorbent filled polymers [20,21]. The basic equation of the model gives the concentration of a species (c, in cm^{3}STP/g)) in the polymer material as follows:

$$c = c_D + c_H = k_D\, p + \frac{C'_H\, b\, p}{1 + b\, p} \qquad (4)$$

where:
k_D : Henry's law solubility coefficient (cm^3 STP/g polymer.bar)
b : hole affinity constant (bar^{-1})
C'_H : hole saturation constant (cm^3 STP/g polymer)
p : pressure (bar)

This equation expresses that the gas molecules are sorbed in two different modes, i.e. according to Henry's law (concentration c_D) and according to a Langmuir equation (concentration c_H). It is assumed that polymers below their glass transition temperatures have inhomogeneities, i.e. there are regions where the polymer chains in their frozen state leave "microvoids" or "holes" in the glassy matrix where gas sorption takes place according to a Langmuir isotherm. It can be immediately observed that such a concept can be applied to zeolite filled polymer membranes since the sorption into a rubbery polymer obeys Henry's law at low pressures and the sorption of gases into zeolites at low pressures can be described by a Langmuir equation.

In the case of zeolite filled membranes, the membrane can be considered as a "black box" and equation (4) can directly be used to model the sorption isotherms. However, it is also possible to incorporate the volume or weight fractions of polymer and zeolite in this equation since they are known. The equation then becomes:

$$c = w_r\, c_D + w_z\, c_H = w_r\, k_D\, p + w_z \frac{C'_H\, b\, p}{1 + b\, p} \qquad (5)$$

where:
w_r : weight fraction of the rubbery polymer (-)
w_z : weight fraction of zeolite (= 1- w_r) (-)

Equations 4 and 5 can be used to model equilibrium sorption isotherms. Transient state sorption and permeation of gases can also be modelled using the dual mode transport theory. However, the model originally postulates that the molecules sorbed in the Langmuir mode are immobilized. This statement is not valid in the case of the zeolite filled membranes presently investigated since it was demonstrated that the molecules sorbed into the zeolite pores indeed contribute to the transport mechanism (chapter III, IV and V of this thesis and reference [22]). An extended model has to be used in the case of zeolite filled polymeric membranes. Such extensions have been published by e.g. Petropoulos [23], Paul and Koros [24], Tshudy et al. [25] and Chern et al. [26]. These extensions account for a partial mobilization of the Langmuir sorbed molecules.

The final equation giving the effective diffusion coefficient of gas molecules into a glassy polymer obtained from the transient state sorption is [24]:

$$D_{eff}(c) = D_D \left[\frac{1 + \dfrac{F K}{(1 + \alpha\, c_D)^2}}{1 + \dfrac{K}{(1 + \alpha\, c_D)^2}} \right] \qquad (6)$$

with: $K = \frac{C'_H b}{k_D}$; $F = \frac{D_H}{D_D}$; $\alpha = \frac{b}{k_D}$

where:
D_D : diffusion coefficient of molecules sorbed in the Henry mode ($cm^2.s^{-1}$)
D_H : diffusion coefficient of molecules sorbed in the Langmuir mode ($cm^2.s^{-1}$)
c_D : local concentration of dissolved penetrant (= k_D p) ($cm^3 STP.g^{-1}$)

In this equation, D_{eff} is determined from the sorption kinetics as explained in appendix 1 of this thesis. F and K are calculated from the dual mode sorption parameters obtained from the equilibrium sorption isotherm. This means that the model contains two fitting parameters: D_D and D_H, the respective diffusion coefficients in the two different phases. The derivation of this equation assumes local equilibrium between the two regions and that both diffusion coefficients D_D and D_H are independent of concentration.

This equation fitted to the experimental results might then give a diffusion coefficient in the zeolite as a result.

VI.3.2- Sorption results and modelling

Sorption equilibrium

SORPTION IN EPDM + SILICALITE-1 (50 wt%)

The sorption isotherms measured at 30°C for carbon dioxide in pure EPDM and in silicalite-1 filled EPDM are given in figure 6.

Again the linear sorption isotherm in the case of unfilled EPDM (Henry sorption) can be noticed and the typical dual mode sorption isotherms in the case of silicalite-1 filled EPDM as well. The Henry solubility constant can be determined for EPDM: $k_D = 0.783$ cm^{3}STP/g polymer.bar. This value and the two weight fractions of zeolite in the polymer are then used, together with equation (5), to calculate the sorption of carbon dioxide in the zeolite itself. Figure 7 shows the result.

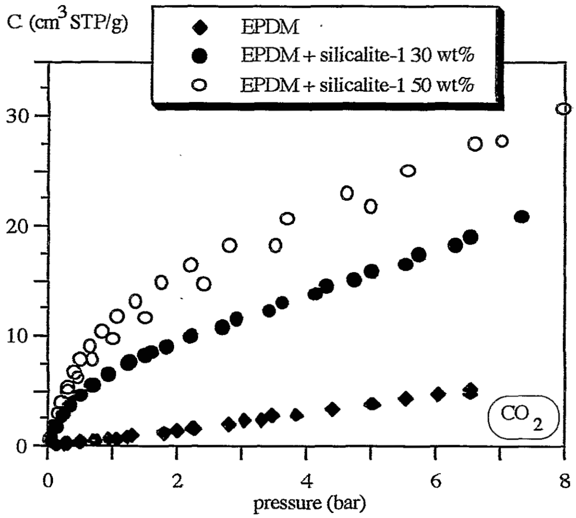

Figure 6: CO_2 sorption isotherm in pure and silicalite filled EPDM at 30°C; vacuum activation at 30°C.

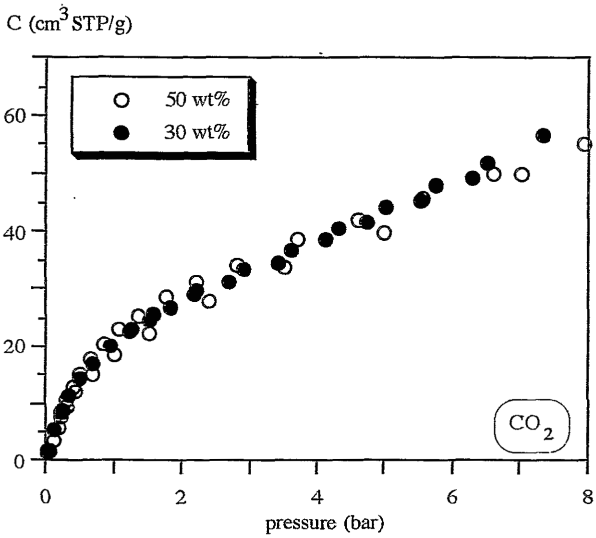

Figure 7: CO_2 sorption isotherm at 30°C in silicalite-1 itself calculated from the sorption data in silicalite-1 filled membranes at 30 and 50 wt% zeolite; vacuum activation at 30°C.

The two different weight fractions of zeolite in EPDM lead to the same sorption isotherm in the zeolite, which is a good indication of the non existence of voids in the membrane.

One must know that the sorption isotherm presented in figure 7 does not really correspond to what can be expected, i.e. the sorption capacity of the zeolite is significantly lower than what is reported in literature [27]. A possible explanation is the incomplete desorption of the zeolite during the activation step, despite indications of complete desorption (see appendix 1 to this dissertation for a more detailed description of the experimental procedure).

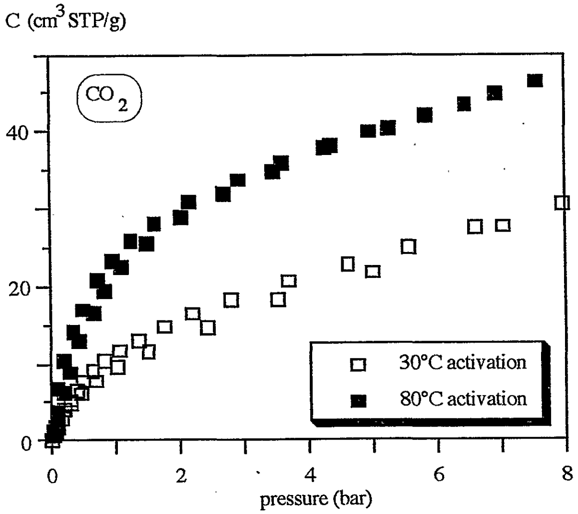

Figure 8: CO_2 sorption in silicalite-1 filled EPDM (50 wt%) using 30°C or 80°C as temperature for vacuum activation.

In order to control this point, a series of experiments was carried out, employing vacuum and a temperature of 80°C as activation procedure. The sorption isotherm in the filled polymer then obtained is shown in figure 8, together with the one measured at 30°C for the same sample (EPDM + silicalite-1 50 wt%). It is clear from figure 8 that a higher activation temperature results in a larger carbon dioxide sorption in the composite membrane, which is due to a more complete desorption of the zeolite pore structure at a higher temperature. The slopes of the linear part of both isotherms are equal, indicating the same sorption into the polymer phase.

The sorption of methane was also measured for the system silicalite-1/EPDM. Figure 9 shows that the sorption of methane is lower than that of carbon dioxide, which is expected since both the polymer and the zeolite are sorption selective for carbon dioxide [27]. In figure 9, the two curves represent the model fit obtained from equation (4) ("black box" approach). The fitting parameters are given in table 3. It is now possible to calculate the sorption of carbon dioxide and methane in silicalite-1 by subtracting from the total sorption in the filled polymer the weighted polymer contribution, as explained previously using equation (5). Figure 10 plots the concentration of carbon dioxide and methane in silicalite-1 as a function of pressure.

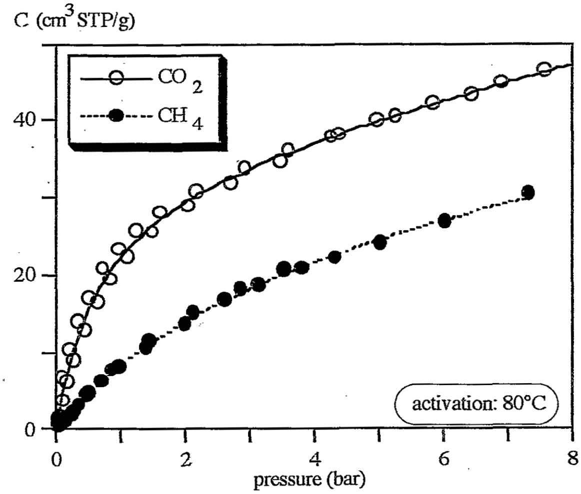

Figure 9: CO_2 and CH_4 sorption in EPDM + silicalite-1 (50 wt%) at 30°C; vacuum activation at 80°C.

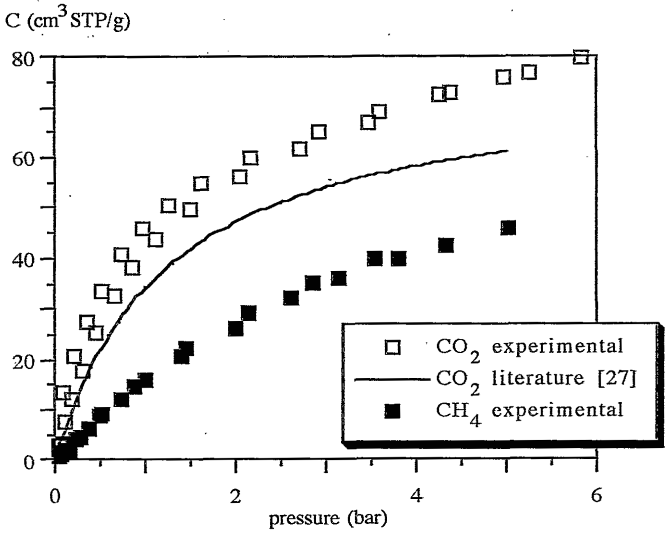

Figure 10: CO_2 and CH_4 sorption in silicalite-1 at 30°C; vacuum activation at 80°C.

It demonstrates that silicalite-1 indeed is CO_2 sorption selective, but the selectivity remains low. In this figure the full curve represents the carbon dioxide sorption in silicalite-1 at 30°C obtained from literature [27]. The sorption calculated from the measurement in silicalite-1 filled EPDM is larger than the literature data. This could be due to the presence of voids in the membrane. Figure 7, however, showed that this is not the case. No explanation for this difference in sorption capacity has been found yet.

Nevertheless, it can be seen that activation under vacuum at 80°C is enough to remove any sorbent from the silicalite-1 structure.

SORPTION IN EPDM + 13X (50 wt%)

Figure 11 shows the sorption isotherms measured at 30°C with carbon dioxide and methane in EPDM filled with zeolite 13X (after vacuum activation at 80°C). The lines represent the dual mode sorption model fit, and the fitting parameters are given in table 3. When comparing this isotherm with what has already been reported in chapter III, one may notice a large difference in sorption capacity. Here the activation conditions are again involved, i.e. the previously reported isotherms were measured after vacuum activation at 30°C, which means that, like in the case of silicalite-1, the zeolite was not totally free of sorbent (water or other components). Especially for hydrophilic zeolites, the activation conditions necessary for the complete removal of water of hydration are so drastic that they cannot be applied to zeolite filled polymers without degradation of the polymer. This means that the zeolite will never be totally desorbed before the sorption experiments start.

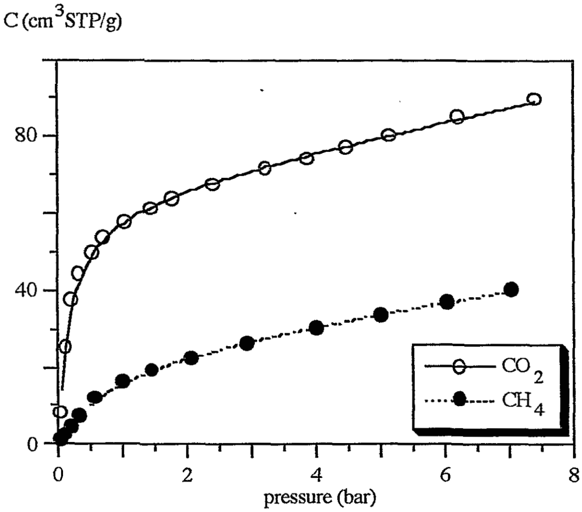

Figure 11: CO_2 and CH_4 sorption in EPDM + 13X (50 wt%) at 30°C.

Figure 12 shows the sorption in the zeolite (calculated by using equation (5)) for carbon dioxide and methane, as well as some literature data (activation at 350°C under vacuum in this case) [28].

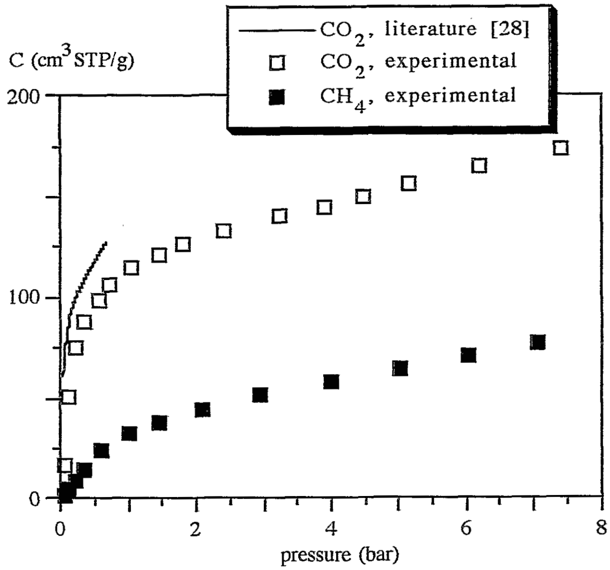

Figure 12: CO_2 and CH_4 sorption in 13X at 30°C from eq.(5).

It is clear that also 13X is sorption selective for carbon dioxide. However, this figure also shows the incomplete desorption of the zeolite prior to the experiments since the curve obtained from literature (where a rigorous desorption step has been applied) clearly indicates a larger sorption capacity for the pure zeolite in the case of carbon dioxide.

SORPTION IN EPDM + 5A (52 wt%)

The sorption of CO_2 and CH_4 in EPDM filled with 5A (52 wt%) was also measured and the results are shown in figure 13 (the lines are model fits, see table 3 for parameters).

The same remark can be made concerning these isotherms, i.e. they show a larger sorption capacity than what has been reported in chapter III. Also here different activation procedures are probably the cause. Figure 14 shows the pure zeolite sorption for CO_2 and CH_4 and literature data for CO_2 sorption. Again, the measured sorption is lower than the isotherm taken from literature, indicating the non-complete desorption of the zeolite 5A before the start of the experiment. Complete desorption of zeolite 5A once incorporated into a polymer phase is obviously not realistic without degrading the polymer.

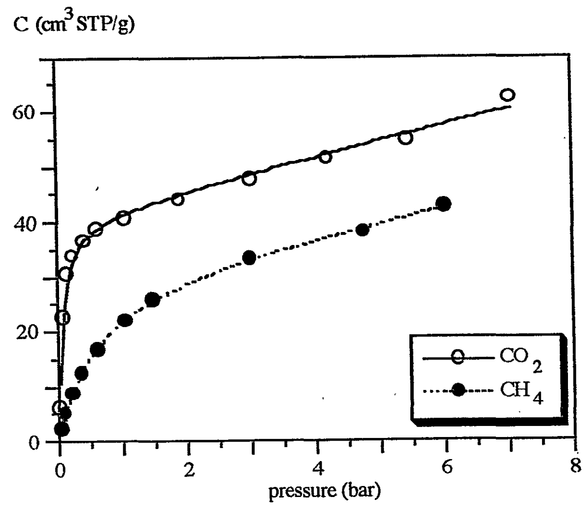

Figure 13: CO_2 and CH_4 sorption in EPDM + 5A (52 wt%) (30°C).

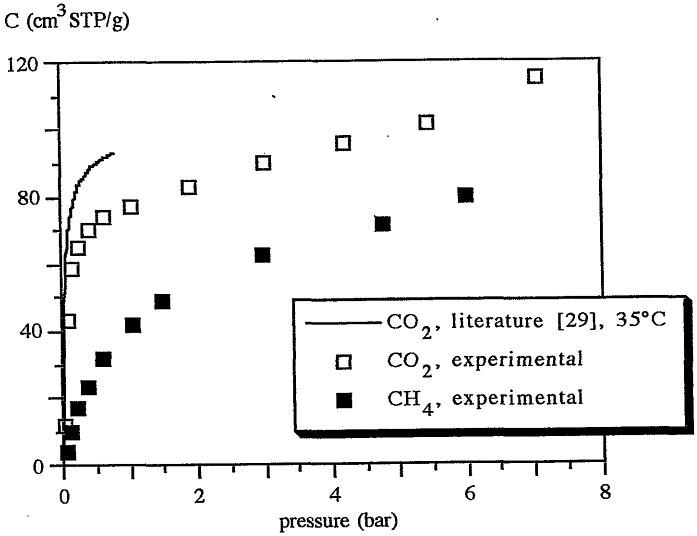

Figure 14: CO_2 and CH_4 sorption in 5A at 30°C making use of eq.(5).

Table 3 shows the dual-mode sorption parameters obtained by modelling the CO_2 and CH_4 sorption isotherms in EPDM and zeolite filled EPDM.

material	gas	k_D ($cm^3STP.g^{-1}.bar^{-1}$)	C'_H ($cm^3STP.g^{-1}$)	b (bar^{-1})
EPDM	CO_2	0.783	-	-
EPDM	CH_4	0.421	-	-
EPDM+silicalite-1	CO_2	1.96	34.25	1.45
EPDM+silicalite-1	CH_4	1.17	31.41	0.29
EPDM+13X	CO_2	3.58	64.19	5.07
EPDM+13X	CH_4	2.52	25.02	1.08
EPDM+5A	CO_2	2.84	40.98	14.18
EPDM+5A	CH_4	2.43	30.51	1.72

Table 3: Dual-mode sorption parameters for various polymer/zeolite/gas systems (30°C).

These parameters clearly reflect the properties of the zeolites. Hydrophilic zeolites (13X and 5A) have high b parameters (hole affinity constant) which indicates a strong interaction between the gas molecules and the polar surface. This effect is much more pronounced for carbon dioxide, as could be expected.

Kinetics of sorption

From the initial slope of the sorption versus the square root of time, an "effective" diffusion coefficient of gas molecules in the membrane can be calculated.
Figure 15 shows this calculated diffusion coefficient versus pressure for unfilled and silicalite-1 filled EPDM.
One can clearly see that the effect of introducing silicalite-1 into EPDM is a decrease of the effective diffusion coefficient, as was already reported in chapter V from time-lag experiments. Furthermore, the pressure dependence of D_{eff} is very large, one order of magnitude, especially in the low pressure range (up to 2 bars). This corresponds to the non-linear part of the sorption isotherm where most of the sorption takes place in the zeolite.

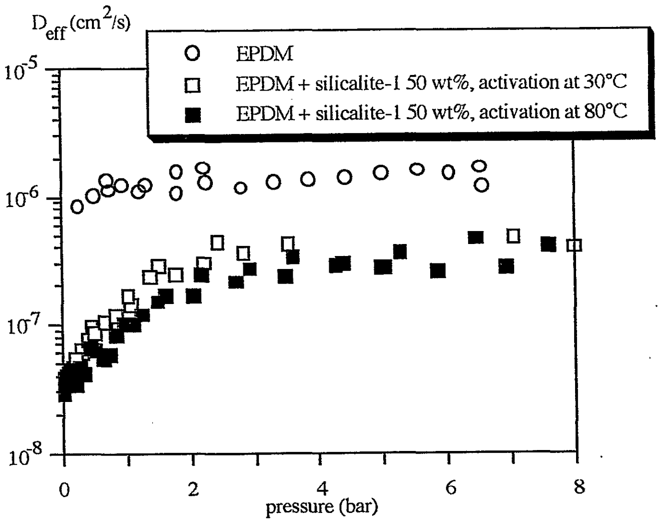

Figure 15: Effective diffusion coefficient obtained from CO_2 sorption kinetics versus pressure in filled (50 wt% silicalite-1) and unfilled EPDM.

Figure 16 gives D_{eff} versus pressure for CO_2 and CH_4 in EPDM filled with 50 wt% of silicalite-1. The effective diffusion coefficient of CH_4 in the composite membrane is lower than the one of CO_2 over the whole pressure range investigated.

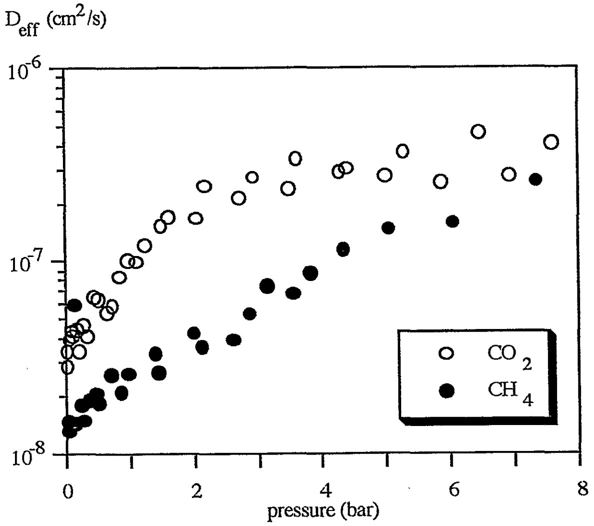

Figure 16: Effective diffusion coefficient of CO_2 and CH_4 in EPDM + silicalite-1 50 wt% versus pressure; vacuum activation at 80°C.

The modelling of such plots is possible using equation (6) and the dual mode sorption parameters obtained from the sorption isotherms and equation (4).

Figure 17 shows the model fit in the case of EPDM filled with silicalite-1 (50wt%) and carbon dioxide.

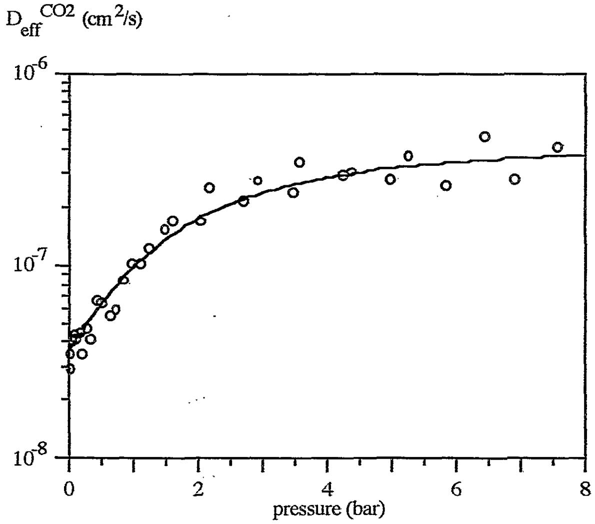

Figure 17: Effective diffusion coefficient of carbon dioxide into EPDM + silicalite-1 (50 wt%) at 30°C; the line corresponds to the model fit using equation (6).

The model fit describes nicely the pressure dependence of the effective diffusion coefficient. The fitting parameters obtained are:

$D_D = 4.32\ 10^{-7}\ cm^2.s^{-1}$
$D_H = 2.1\ 10^{-8}\ cm^2.s^{-1}$

The diffusion coefficient in silicalite-1 D_H may be compared to literature data. However, most of the diffusion studies on silicalite-1 and ZSM-5 deal with molecules like benzene, xylenes and paraffins. This means that no diffusion coefficient values of carbon dioxide in silicalite-1 are known to be compared with the value we have found. Hayhurts et al. reported on the diffusion of methane through silicalite-1 in a single crystal [30]. They report a diffusion coefficient of 1.1 10^{-6} $cm^2.s^{-1}$ for methane at 61°C. The activation energy of diffusion of methane in silicalite is about 4 kJ/mol [31,32]. This means that at 30°C, the diffusion coefficient of methane would be about 9.5 10^{-7} $cm^2.s^{-1}$, which is about 50 times larger than the value obtained for carbon dioxide in our study. Carbon dioxide has a smaller kinetic diameter than methane (3.3 and 3.8 Å respectively). This means that a larger diffusion coefficient should be found for carbon dioxide than for methane in a zeolite framework like silicalite-1 where the interactions sorbate-sorbents are weak.
It must be considered, though, that the measurement of transport diffusivities of molecules in zeolites yields results with very large discrepancies. This might be due to extracrystalline transport resistances, heat effects or surface barrier

effects [33]. The diffusion coefficient of methane in silicalite-1 obtained by a chromatographic method yields a value of 10^{-10} $cm^2.s^{-1}$ [33], which means 4 orders of magnitude lower than values obtained from the membrane technique [30]. On the other hand, self diffusion coefficients can be determined in the range 10^{-4}-10^{-5} $cm^2.s^{-1}$ [31,32]. Therefore, it is difficult to state whether the diffusion coefficient obtained from the model is correct or not.

Furthermore, one should more carefully consider the exact meaning of D_D and D_H values. If the transport through the zeolite filled membrane is considered in terms of jumps from site to site, a diffusing molecule might jump from a site in the polymer to another one in the polymer (D -> D), from the polymer to the zeolite (D -> H), inside the zeolite (H -> H) or from the zeolite to the polymer (H -> D). This means that D_H is actually a coefficient of diffusion of molecules with a surface barrier which is due to the presence of the polymer phase around the zeolite particles, and not of the gas phase as normally is the case in sorption and diffusion studies. It is known that such a surface barrier can be responsible for a large decrease of the sorption rate into the zeolite, and as a result, the measured diffusion coefficient using filled membranes can be much lower than the actual intracrystalline diffusion coefficient [33].

VI.4- Activated permeation

As has already been shown in chapter V of this thesis, the permeation of gas molecules through zeolite filled polymeric membranes can be considered as an activated process, which means that an activation energy of permeation can be defined and determined. Furthermore, the permeability of the zeolite filled polymer system versus the volume faction of zeolite can be described using for example the geometrical mean relation (equation (1)) as was previously demonstrated in this chapter (see figure 3).

The good fit obtained in figure 3 means that the following relation can be written for the range of temperatures investigated (0-30°C):

$$\ln(P^o \exp(-E_p / RT)) = \phi_z \ln(P^o_z \exp(-E_{p,z} / RT)) + (1 - \phi_z) \ln(P^o_r \exp(-E_{p,r} / RT)) \qquad (7)$$

which means that after rearrangement equation (8) is obtained:

$$E_p = \phi_z E_{p,z} + (1 - \phi_z) E_{p,r} \qquad (8)$$

This relation shows that the activation energy of permeation of the silicalite-1 filled membranes should be linearly dependent on the zeolite volume fraction and with a slope equal to $(E_{p,z} - E_{p,r})$.
Figure 18 shows the activation energy of permeation of carbon dioxide through silicalite-1 filled membranes as a function of the silicalite-1 volume fraction.

The line, a model fit using equation (8), is straight and describes reasonably well the experimental points. The resulting parameter $E_{p,z}^{CO_2}$ is an activation energy of permeation of carbon dioxide through silicalite-1.

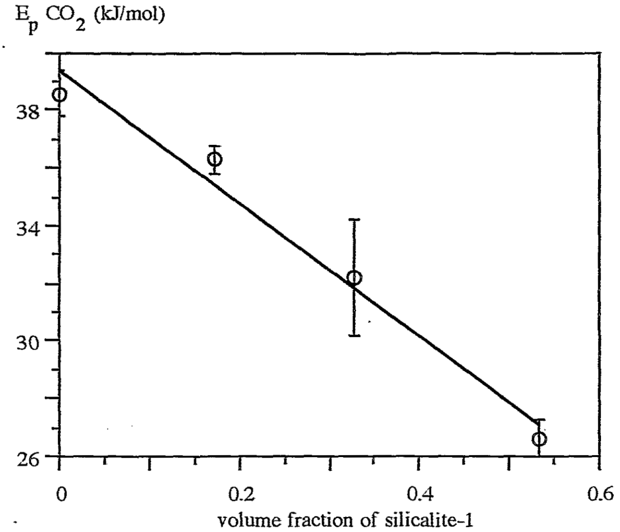

Figure 18: Activation energy of permeation versus volume fraction of silicalite-1 in EPDM in the case of carbon dioxide; the line represents a linear regression through the points.

The result is a value of E_p^{CO2} $_{(silicalite-1)} = 15.6 \pm 5$ kJ/mol, which is much lower than the value of the pure polymer (38.6 kJ/mol). This number should be compared to reported values. Unfortunately, the permeation of carbon dioxide through a single silicalite-1 crystal or a silicalite-1 membrane has not been reported yet. The value obtained, if correct, means that the zeolite permeability increases with temperature in the range investigated. This indicates that the decrease in sorption capacity due to the temperature increase (as shown in reference [27]) is overcompensated by the faster diffusion of CO_2 molecules through the zeolite pores. It also means that the permeation of carbon dioxide through silicalite-1 is less dependent on temperature than in a polymer like EPDM.

VI.5- Separation Power

In order to compare the separation abilities of various polymers for a given mixtures, one can define a Separation Power (S.P.) as follows:

$$S.P. = P_{CO_2} * \alpha_{CO_2/CH_4} \quad \text{(Barrer)} \qquad (9)$$

It allows to integrate in one number both permeability and selectivity. This number was calculated for various zeolite filled membranes (see figure 19) as a function of the zeolite volume fraction.

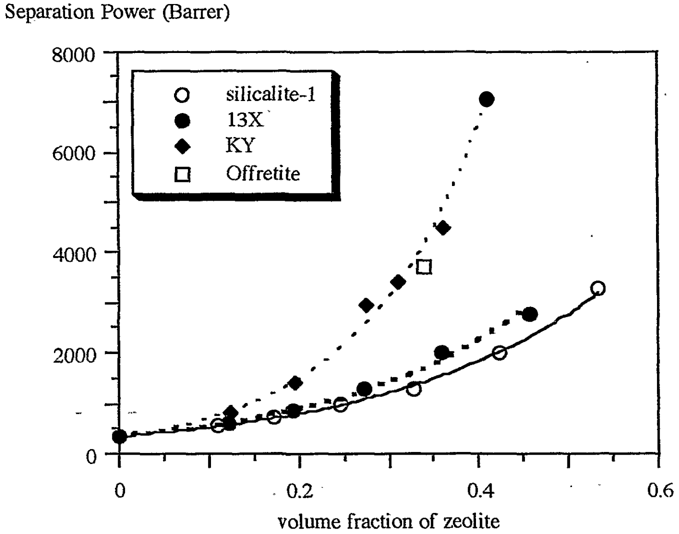

Figure 19: Separation power of various zeolite filled EPDM membranes versus volume fraction of zeolite (CO_2/CH_4); the curves are exponential fits.

The zeolites 13X and silicalite-1 result in about the same separation power at a given volume fraction. KY and Offretite show much larger improvement of the separation power.

Extrapolating the exponential curve fit to volume fraction 1 gives what could be considered as the zeolite separation power for the mixture CO_2/CH_4. Table 4 shows the results.

zeolite	silicalite-1	13X	KY
S.P. (Barrer)	22248	37238	540267

Table 4: Separation Power of zeolites obtained by extrapolation to volume fraction 1 in figure 19.

Again, as was explained in a previous section, these zeolite separation powers are not intrinsic properties, they are dependent on the polymer phase present around the zeolite particles. These numbers only allow to draw a scale of performance of various zeolites with respect to their effect on the gas separation properties for one polymer: EPDM. A new scale should be applied for another polymer phase, which would give the same classification (see chapter III) but different numbers.

In chapter I, a plot of carbon dioxide permeability versus selectivity for carbon dioxide over methane was given. Simply considering the polymers investigated in our study, figure 20 shows the same plot with unfilled and filled polymers.

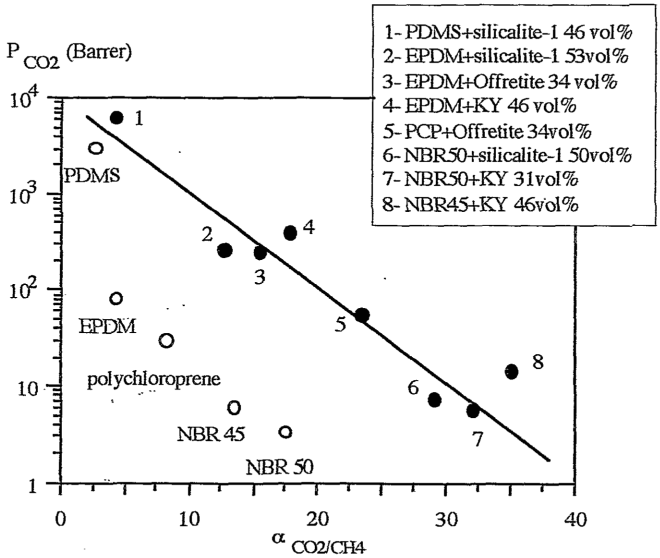

Figure 20: CO_2 permeability versus CO_2/CH_4 selectivity for unfilled and zeolite filled rubbery polymers.

This graph shows that the trade-off curve is moved towards the region of higher permeability and selectivity. This clearly shows that the incorporation of certain zeolites results in a large improvement of the separation power by increasing both selectivity and permeability.

VI.6- Conclusions

Permeability models defining a specific zeolite permeability describe the gas permeation results obtained for the system EPDM/silicalite-1 quite well. However, the zeolite permeabilities determined in this way appear not to be intrinsic properties of the zeolite, i.e. they are dependent on the polymer phase present around the particles. The assumptions of the permeability models that the permeation behaviour of the individual parts, polymer and zeolite, remains the same and independent of each other is thus not correct for zeolite filled polymer membranes.

The dual mode sorption model can be applied to the sorption of gases into zeolite filled polymers. The kinetics of sorption modelled with the extended dual mode transport model yields a diffusion coefficient in the "holes" which could be compared to diffusion coefficients in zeolites from literature. However it does not represent exactly the diffusion coefficient in the zeolite, since the model assumes concentration independency, which is most of the time not valid in zeolites. It is an average value over the whole concentration profile in the membrane which also takes into account possible surface barrier effects due to the presence of the polymer phase.

List of symbols

b	hole affinity constant	bar^{-1}
c	concentration of gas	$cm^3STP.g^{-1}$
C'_H	hole saturation constant	$cm^3STP.g^{-1}$
D	diffusion coefficient	$cm^2.s^{-1}$
E	activation energy	$kJ.mol^{-1}$
k_D	Henry's solubility coefficient	$cm^3STP.g^{-1}.bar^{-1}$
p	pressure	bar
P	permeability coefficient	Barrer
R	gas constant	$J.mol^{-1}.K^{-1}$
S.P.	separation power	Barrer
w	weight fraction	-
ϕ	volume fraction	-
α	selectivity	-

subscripts

D	in the Henry's mode
eff	effective (diffusion coefficient)
H	in the Langmuir mode
i	component i
p	permeation
r	rubber
z	zeolite

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Appendix to chapter VI
Critical discussion of Petropoulos and te Hennepe's models

Te Hennepe's model is used in this thesis (chapter II and in the present chapter) to model the results. Despite a good fit with the experimental data, this model seems to be not completely correct. The equation derived by te Hennepe is:

$$J_i = \Delta p_i \Big/ \left(\frac{(1 - \phi_z^{1/3})\, d}{P_{r,i}} + \frac{3/2\, \phi_z^{1/3}\, d}{P_{r,i}\,(1 - \phi_z) + 3/2\, P_{z,i}\, \phi_z} \right) \qquad (10)$$

If two different materials having the same permeability are mixed, the membrane prepared in this way is expected to have the same permeability as a membrane prepared directly from one of the pure material. However, studying equation (10) with $P_{r,i} = P_{z,i}$, one can see that the resulting flux is not the pure polymer flux, but that a function of the filler volume fraction remains:

$$J_i = \frac{\Delta p_i\, P_{r,i}}{d} \Big/ \left(1 - \phi_z^{1/3} + \frac{3/2\, \phi_z^{1/3}}{1 + 1/2\, \phi_z} \right) = J_i^{\,pure} * f(\phi_z) \qquad (11)$$

Figure 21 shows the "deviation function" $f(\phi_z)$ as function of the volume fraction of filler.

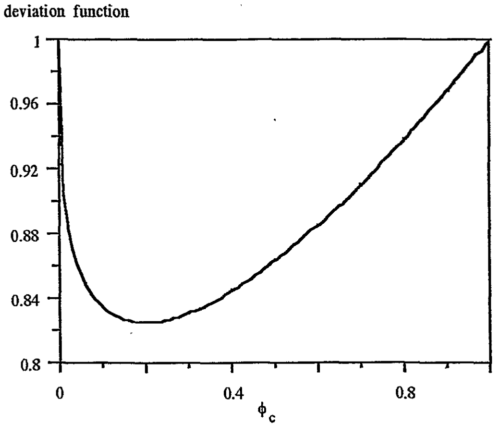

Figure 21: Deviation function obtained when $P_{r,i} = P_{z,i}$

Furthermore, the application of equation (2) to the experimental results obtained with zeolite KY is not possible. The model does not converge towards a "zeolite permeability". The same is observed when using equation (3) (Petropoulos). Only the geometrical mean relation (equation (1)) can describe the results. This equation is equivalent to an exponential fit of the plot permeability versus zeolite volume fraction. It gives a carbon dioxide permeability equal to 4060 Barrer and a selectivity of 133 for zeolite KY when incorporated into EPDM.

Appendix 1

Experimental aspects

This appendix gives a more detailed description of the experimental and calculation methods which were used to obtain the results presented in the former chapters. The following methods are considered here: pervaporation, gas permeation and gas sorption.

A1.1- Pervaporation

Pervaporation experiments can be carried out in different ways, the main differences being the methods used to apply the driving force and collect the permeate (vacuum, sweep gas, cold trap). Figure 1 gives a schematic representation of the experimental set-up used in this study.

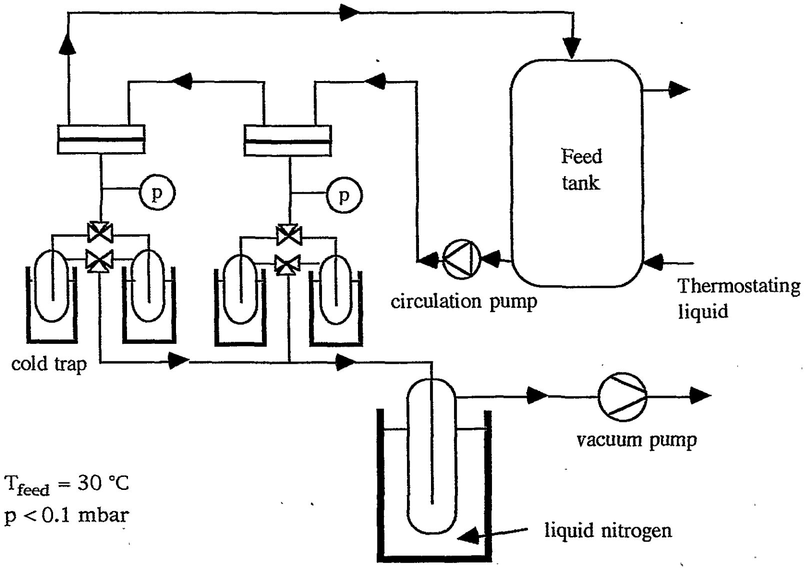

Figure 1: Schematic representation of the pervaporation set-up.

The feed mixture consists of a solution of 10 weight% of toluene in ethanol. The membranes are immersed in the feed before being mounted in the pervaporation cells. The surface area of the membrane in contact with the feed mixture is 28.3 cm^2. The volume of the feed mixture used was large enough to avoid significant composition variations during a pervaporation experiment. When necessary the composition of the feed mixture was readjusted to the desired value.

Once the membrane was mounted in the cell and the driving force applied, a period of 2 to 3 hours was allowed for reaching a stationary state before really starting a measurement. The permeate was then collected in one of the cold traps filled with liquid nitrogen. The weight of permeate collected within a certain time interval gave the total flux through the membrane. The permeate, as well as a sample of the feed mixture, were analysed by gas chromatography using a Varian 3400 chromatograph with a HayeSep Q column. From these analyses, the selectivity could be calculated. The collection of samples was carried out several times over a period of 2 to 4 days to assure steady-state conditions.

The flux was then normalized to a thickness of 100 µm assuming a linear relationship between the flux and the inverse of the membrane thickness:

$$J_{100\mu m} = J.d/100 \ (g.m^{-2}.h^{-1}) \tag{1}$$

where d is the actual thickness of the dense membrane (µm).

The selectivity α was calculated as follows:

$$\alpha_{\text{toluene / ethanol}} = \frac{\left(\frac{x_{\text{toluene}}}{y_{\text{ethanol}}}\right)_{\text{permeate}}}{\left(\frac{x_{\text{toluene}}}{y_{\text{ethanol}}}\right)_{\text{feed}}} \tag{2}$$

where x and y are weight fractions.

A1.2- Gas permeation

The gas permeation set-up is briefly described in figure 2. It is basically the same as described in references [1] to [3]. Only one permeation cell is given here for simplicity. The feed gas is streamed at the upstream side of the membrane at a rate of 10 to 20 ml/min. The feed pressure could be adjusted within a range of 1 to 8 bars (absolute). The downstream side of the membrane was kept under vacuum, i.e. at a pressure lower than 0.1 mbar. Carbon dioxide (>99.99%), methane (>99.99%), argon, helium, nitrogen and oxygen (>99.95%) were used as gases. The experiments were normally carried out at room temperature. To study the influence of temperature on the selectivity and permeability a double-walled cell was used.

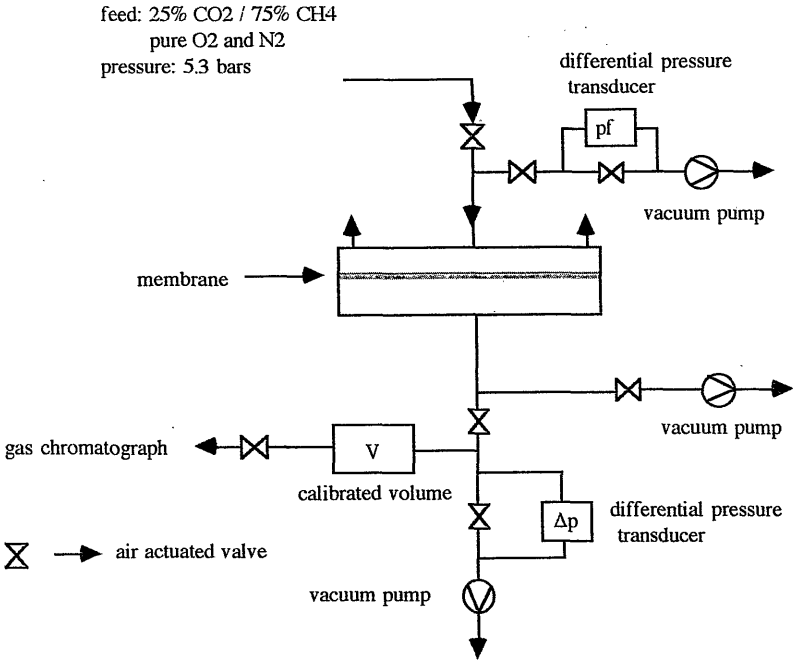

Figure 2: Schematic representation of the gas permeation set-up.

The permeability was determined by a measurement of the pressure increase in a calibrated volume by means of a low pressure Baratron differential pressure transducer. The selectivity was determined by gas chromatography analysis of the feed and the permeate in the case of CO_2/CH_4 (Varian 3200 gas chromatograph) and from the ratio of pure gas permeabilities in other cases. The measurement volume was calibrated with a standard polyester film (Standard Reference Material 1470) of the National Bureau of Standards in Washington D.C. (USA).

The carbon dioxide permeability and selectivity were calculated with equations (3) and (4). Here it is assumed that gases behave ideally and that the change in permeate pressure during the pressure increase measurement is negligible in comparison with the feed pressure:

$$(P/l)_{CO_2} = V\, x_{CO_2,p}\, \Delta p \,/\, (A\, x_{CO_2,f}\, p_f\, \Delta t\, 76) \tag{3}$$

$$\alpha_{CO_2/CH_4} = [x_{CO_2,p} \,/\, (1 - x_{CO_2,p})] \,/\, [x_{CO_2,f} \,/\, (1 - x_{CO_2,f})] \tag{4}$$

with:

$(P/l)_{CO_2}$	gas flux for CO_2	$(cm^3(STP).cm^{-2}.s^{-1}.cmHg^{-1})$
V	calibrated volume	(cm^3)
$x_{CO_2,p}$	CO_2 content in the permeate	(vol%)
Δp	pressure increase in the calibrated volume during Δt	(mmHg)
A	membrane surface area	(cm^2)

$x_{CO_2,f}$	CO_2 content in the feed	(vol%)
p_f	feed pressure	(mmHg)
Δt	time necessary to reach a pressure increase Δp	(s)
76	pressure correction factor	(cmHg)

The same permeability equation was used to calculate the pure gas permeabilities with $x_{i,p} = x_{i,f} = 1$.

The characterization of a membrane was carried out over a period ranging from one day to one week depending on the type of adsorbent and the polymer used. The selectivity and permeability were measured at regular time intervals at steady-state conditions.

A1.3- Gas sorption

The sorption isotherms were determined by a pressure decay method. This method is well described in references [2], [4] and [7]. The experimental set-up is represented in figure 3.

In this method, the sample to be characterized is placed in a cell connected to a perfectly symmetric reference cell (empty) via a Differential Pressure Transducer (DPT, Valydine DP15). The two cells are evacuated to a pressure of 0.1 Pa at room temperature for at least one night in order to remove all sorbed gas molecules from the sample. Then the cells are isolated from the feed line and are only connected via the DPT (V1 and V2 are closed). No pressure difference is observed when the sample has been degassed correctely.
The pressure of the feed gas can then be adjusted in the cells via two feed lines (one from 0 to 2 bars absolute and the other from 1 to 8 bars absolute, pressure reading via a Transinstruments pressure transducer). At initial time t_0 the two isolation valves V1 and V2 are simultaneously opened and closed again after a short while which allows the gas pressure to settle in the cells. Because of sorption in the sample, a pressure difference is created and is recorded via the DPT. The experiment is then carried out until the pressure difference remains constant. At this moment, the pressure above the cells is set to a higher value and the same operations as above are carried out. It is possible to determine the sorption isotherm step by step in this way.

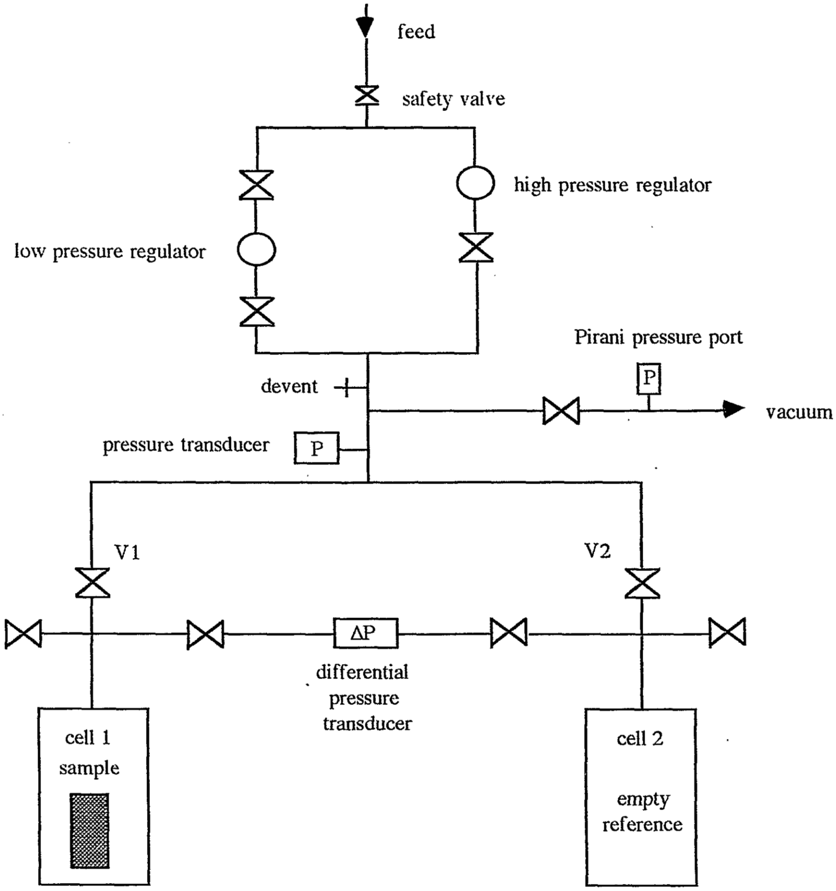

Figure 3: Schematic representation of the gas sorption set-up.

Figure 4 shows a typical sorption curve as well as the principle of the calculation procedure. Because the time necessary to adjust the new pressure in the cells is not negligible, one has to extrapolate the sorption uptake which was not recorded during this time. This is done by assuming a square root of time dependence of the relative uptake and extrapolating the linear part of the graph to initial time t_0. The pressure difference recorded can then be corrected to obtain the actual sorption uptake.

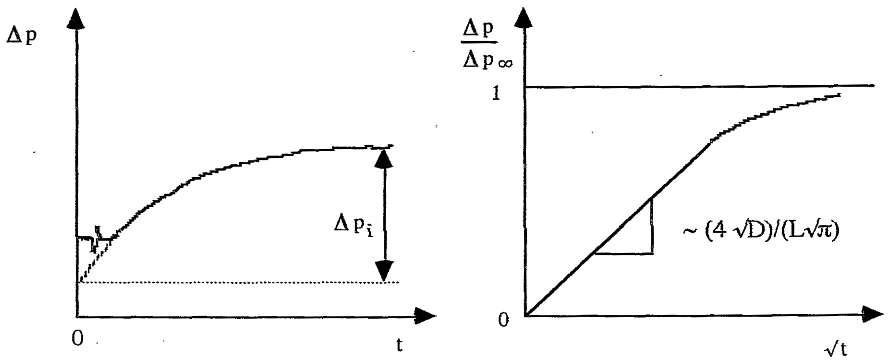

Figure 4: Schematic view of the output signal and calculation procedure.

The concentration change $\Delta c_i = (c_i - c_{i-1})$ (cm^3 (STP)/g) in the sample resulting from an increase of the equilibrium pressure from p_{i-1} to p_i is calculated from the recorded pressure difference Δp_i (Pa) using the following equation and assuming ideal gas behaviour:

$$\Delta c_i = \Delta p_i * (V_{mol}^{\ gas}(STP) \ / \ m)*(V_{cell} - V_{sample}) \ / \ (RT) \qquad (5)$$

with:

$V_{mol}^{\ gas}$	molar volume of a perfect gas at 1atm, 0°C (22414 cm^3)
V_{cell}	volume of the cell (cm^3)
V_{sample}	volume of the sample (cm^3)
m	weight of the sample (g).
R	universal gas constant (J.mol^{-1}.K^{-1})
T	experimental temperature (K)

and the total concentration c_j at equilibrium pressure p_j is given by:

$$C_j = \sum_{i=1}^{j} C_i \qquad (cm^3 \ (STP).g^{-1}) \qquad (6)$$

The effective diffusion coefficient is calculated from equation (7), in which k is the initial slope of the curve representing the relative sorption versus the square root of time and l the membrane thickness (cm):

$$D_{eff} = \pi \ (k^*l \ / \ 4)^{\ 2} \qquad (cm^2.s^{-1}) \qquad (7)$$

This equation is valid for the diffusion of a penetrant molecule into a plane sheet [5,6].

It is also possible to use equation (8) to calculate the effective diffusion coefficient:

$$D_{eff} = 0.049/(t/l^2)_{1/2} \qquad (cm^2.s^{-1}) \qquad (8)$$

where $(t/l^2)_{1/2}$ corresponds to the half-time of sorption. This equation is valid if the sorption curve plotted as a function of the square root of time is linear up to 50% of the total sorption [5,6].

Both equations assume a constant diffusion coefficient (independent of concentration). However, the experiments carried out in this study showed that this is not always the case for the systems investigated. Nevertheless the method consisting of measuring the sorption isotherm step by step allows to calculate a mean effective diffusion coefficient in the corresponding concentration interval in the membrane.

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Appendix 2

On the preparation of zeolite filled glassy polymer membranes

A2.1- Introduction

In chapter III it was mentioned that the filling of glassy polymers with zeolites was investigated without succeeding in preparing a defect-free internal structure.

In this appendix an overview is given of the various glassy polymers investigated and the internal structures obtained by the normal casting-evaporation process. The different experimental methods applied to improve the internal structure are then individually described and the results are given. Finally, some conclusions are drawn and directions for further investigation are given.

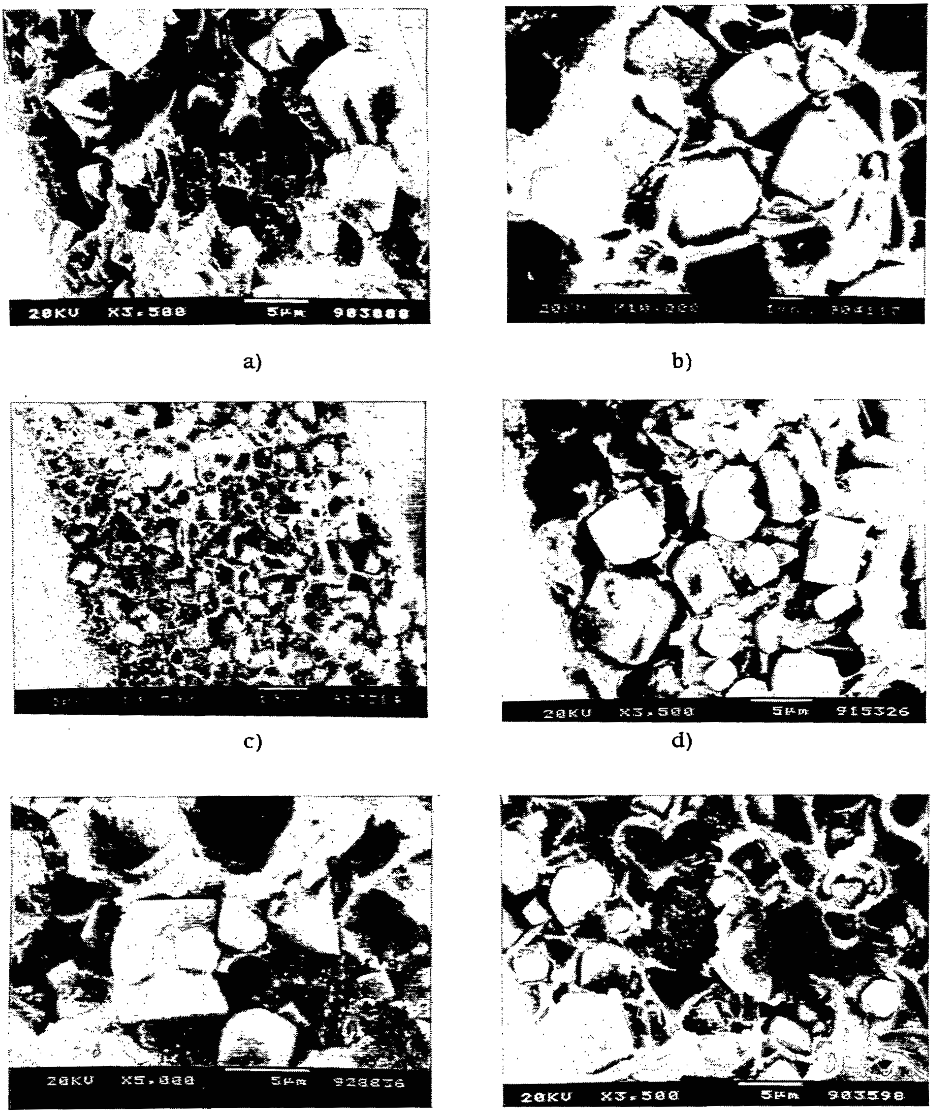
A2.2- Casting evaporation

This preparation method is similar to the one used for rubbery polymers. Table 1 gives a list of polymers used. They are in the glassy state at room temperature, except for the inorganic polyphosphazene ADP 300.

polymer name (abbreviation)	Tg (°C)	commercial name and origin
cellulose acetate (CA)	80	Aldrich
polysulfone (PSF)	110	Udel P3500, Amoco
polyetherimide (PEI)	210	Ultem, General Electric
poly(4-methyl-1-pentene) (TPX)	36	TPX MX001, Mitsui
poly(2,6-dimethyl-p-phenylene oxide) (PPO)	210	General Electric
polyimides (PI)	315	PIXU 218, Ciba Geigy
	310	UPJOHN 2080
polydiphenoxyphosphazene	0	ADP 300, Atochem

Table 1: Overview of polymers used (see appendix 3 for the chemical structures).

The experimental procedure consisted of dissolving the polymer in a suitable solvent and adding the desired amount of zeolite. After one night stirring at least, the solution was cast on a glass or a Teflon™ plate and the solvent was allowed to evaporate in a nitrogen atmosphere. The membranes were further dried in a vacuum oven. Figure 1 gives typical examples of internal structures observed for different polymers with silicalite-1 as zeolite.



a) b)

c) d)

e) f)

Figure 1: SEM photograph of the cross-section of zeolite filled polymer membranes, a) CA + silicalite-1 25wt% (x3500); b) PEI + silicalite-1 25 wt% (x10000); c) PPO + silicalite-1 50 wt% (x1500); d) TPX + silicalite-1 40 vol% (x3500); e) ADP 300 + silicalite 50 wt% (x5000); f) PSF + silicalite-1 20wt% (x3500).

It can be seen from figure 1 that in all cases the adhesion between the polymer and the external surface of the zeolite is very bad. The use of an inorganic polymer like the polyphosphazene did not give any better result, probably due to the crystallinity of this rubbery polymer [1].

It is quite obvious that membranes with such an internal structure consist of three phases instead of two: polymer, zeolite and voids around the particles. Table 2 gives some gas permeation results obtained with zeolite filled glassy polymer membranes prepared by a simple casting-evaporation process in comparison with the results obtained with unfilled polymers.

membrane	P_{CO_2} (Barrer)	α_{CO_2/CH_4}
CA (from acetone)	11	41
CA + silicalite-1 25 wt%	18	40
PEI (from NMP)	1.5	61
PEI + silicalite-1 50 wt%	14.6	34
PEI + KY 50 wt%	95	43
TPX (from TCE)	71	6.8
TPX + silicalite 30 vol% (from TCE)	154	9.1
TPX (from PCE)	57	7.8
TPX + silicalite-1 30 vol% (from PCE)	103	8.6

Table 2: Gas separation results obtained with zeolite filled and unfilled glassy polymer membranes (NMP: N-methyl-2-pyrrolidone, TCE: trichloroethylene, PCE: perchloroethylene).

It can be observed that little or no improvement at all is obtained. In general, the gas permeability increases when zeolite particles are added, but the selectivity decreases or remains about the same. This may be due to the fact that the zeolite is less selective and more permeable than the polymer phase. However, figure 1 clearly shows that this is more likely the results of the interphase voids which drastically increase the permeability without affecting or decreasing the selectivity, except in the case of TPX for which a slight increase in selectivity is observed.

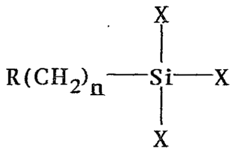
Various methods were investigated to improve the internal structure of these membranes.

A2.3- Surface modification of the zeolite external surface

A2.3.1- Principle

Problems of adhesion and wetting between an organic and an inorganic phase are encountered in many fields. As an example the adhesion of polymer films to a metal substrate or to glass fibers can be mentioned. Our situation is quite similar to this except that the substrate consists of a powder.

One way to solve this problem is to modify the surface properties of the substrate to make it more compatible to the organic phase. This can be achieved, for instance, by grafting some organic chains onto the inorganic surface by means of silane coupling agents. For a complete description of this concept, one is referred to the excellent book of E.P.Plueddeman [2], a pioneer in this field, and to references [3] to [8]. The general chemical structure and the basic principle are shown in figures 2 and 3.



$R(CH_2)_n\text{—}\overset{X}{\underset{X}{Si}}\text{—}X$

X = hydrolyzable group, e.g. OMe, OEt,

R = organofunctional group, e.g. amino, epoxy

Figure 2: General chemical structure of silane coupling agents.

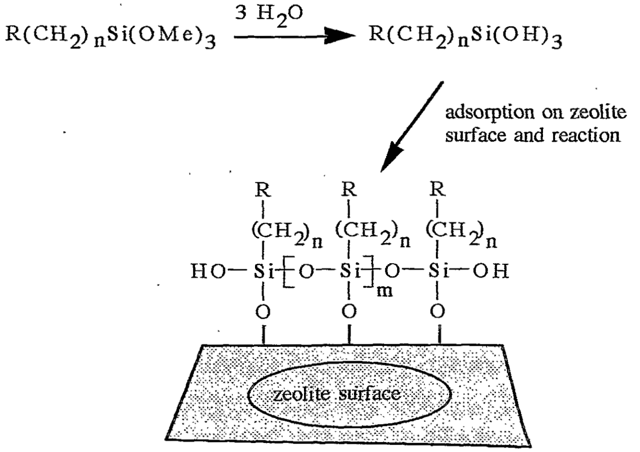


Figure 3: Principle of coupling of organofunctional silanes onto zeolite surface.

The methoxy (or ethoxy) groups are first hydrolysed by water traces followed by a condensation reaction with hydroxyl groups (silanol) present at the external surface of the zeolite particle.
In this study, amino functional silanes were investigated.

A2.3.2- Experimental

Figure 4 shows the different silane coupling agents which were used.

The experimental procedure to modify the external surface of the zeolite was adapted from reference [9]. The silane coupling agent is mixed with toluene and then the zeolite is added. The reacting mixture is then heated up to 70°C and stirred overnight. After filtration and thoroughly washing with methanol to remove unreacted silane, the zeolite is dried at 80°C in air and then placed in a vacuum oven at room temperature.

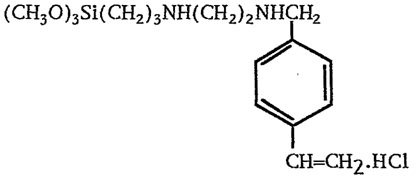
chemical structure	commercial name and manufacturer
$H_2N(CH_2)_3Si(OCH_2CH_3)_3$ γ-aminopropyltriethoxy silane	A-1100 (Union Carbide)
$H_2N(CH_2)_2NH(CH_2)_3Si(OCH_3)_3$ N-β-(aminoethyl)-γ-aminopropyltrimethoxy silane	A-1120 (Union Carbide)
 $(CH_3O)_3Si(CH_2)_3NH(CH_2)_2NHCH_2-C_6H_4-CH{=}CH_2.HCl$ Styryl amine functional silane	Z-6032 (Dow Corning)

Figure 4: Chemical structures and names of the silane coupling agents used in this study.

To determine whether the modification had actually taken place, two analysis methods were used. The first one was elementary analysis. The detection of more carbon and nitrogen than in non-modified silicalite indicated that indeed some coupling agent remained attached to the zeolite surface (table 3).

zeolite	Al (wt%)	Si (wt%)	C (wt%)	N (wt%)	H (wt%)
silicalite 1 before calcination	0.08	45	0.08 (±0.04)	0.03 (±0.02)	0.24 (±0.04)
silicalite-1 after calcination	0.34	44.6	0.04 (±0.03)	0.07 (±0.02)	0.19 (±0.03)
silicalite-1 + A-1120	0.21	41.6	6.31 (±0.02)	1.07 (±0.02)	0.85 (±0.03)
silicalite-1 + A-1100	0.35	43.8	3.5 (±0.06)	0.10 (±0.02)	0.49 (±0.03)

Table 3: Elementary Analysis of silicalite-1 before and after coupling.

The second analysis method was Electron Spectroscopy for Chemical Analysis (or X-ray Photoelectron Spectroscopy). The apparatus used was a Kratos XSAM 800 with a Mg anode (15kV, 15 mA). The zeolite powder was spread on an adhesive aluminium tape, pressed and the excess powder was removed. The sample was then evacuated at 10^{-9} mmHg at room temperature. This method only gives results about the outer surface of the zeolite particles since the method allows for a maximum measuring depth of 100 Å. Figure 5 shows a typical XPS spectrum for silicalite-1 powder before and after coupling with agent A-1120.

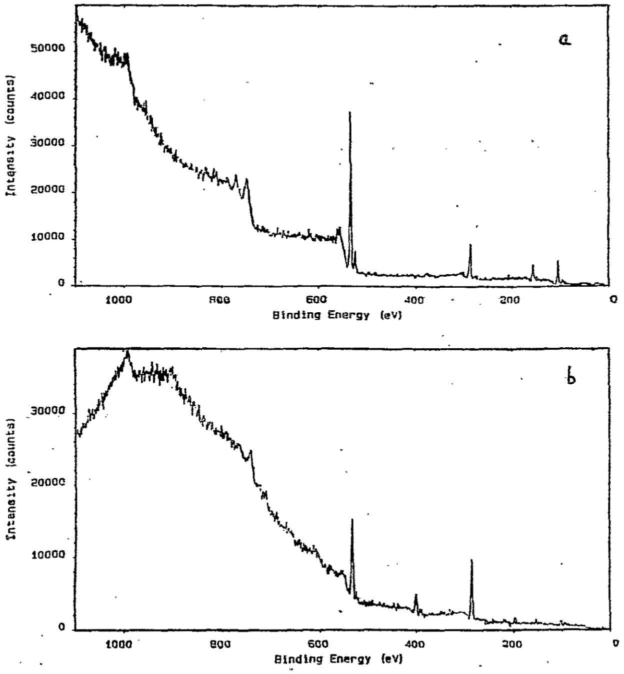


Figure 5: XPS spectrum of silicalite-1 powder before (a) and after (b) coupling with agent A-1120.

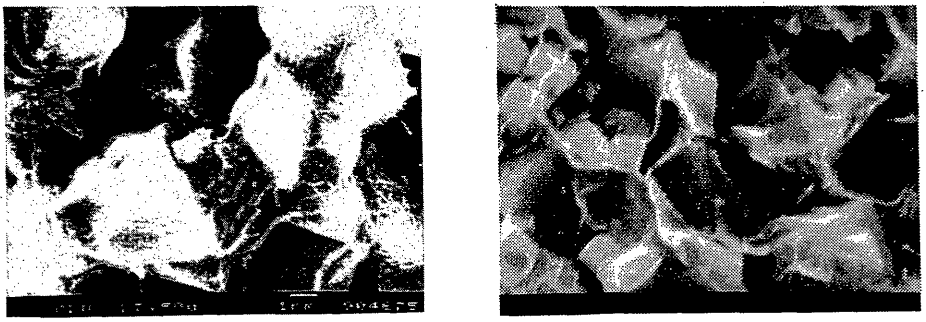
It can be seen that a peak appears at a binding energy of about 400 eV when the zeolite is treated with A-1120. This peak is representative of the nitrogen atoms of the amino silane. This means that some molecules of the silane coupling agent were grafted onto the external surface of the zeolite and that the results obtained by elementary analysis which also show the presence of nitrogen atoms are not only due to silane molecules which may be sorbed into the zeolite pores (these would not be detected so well by surface analysis).

A2.3.3- Results and discussion

The previous paragraph gave strong evidence that coupling of the silane agent took place at the external surface of silicalite-1. The next step of the study was then to investigate whether this surface modification had any effect on the internal structure of a silicalite-1 filled glassy polymer membrane.

Scanning Electron Microscopy (SEM)

Figure 6 shows two examples of PEI filled with a modified silicalite-1 (with A-1100 and A-1120 agent respectively).



a) b)

Figure 6: SEM photographs of PEI membranes filled with 25 wt% of silicalite-1 modified with a) A-1100 (x7500) and b) A-1120 (x5000); the membranes were prepared with n-methyl pyrrolidone (NMP) as solvent.

By comparing these two photographs with figure 1b) it becomes very clear that the presence of coupling agent improves to a large extent the internal structure of the membrane. These membranes were prepared with 25 wt% of zeolite. However, the low density of the solvent (NMP, $\rho = 1.03$ g/cm^3) compared to the zeolite density (1.76 g/cm^3) and the low polymer concentration (15 wt%) resulted in sedimentation of the zeolite particles. The actual zeolite weight fraction in the layer where zeolite can be seen is thus much larger than 0.25 (an estimation based on the thickness of the membrane where zeolite is present relative to the total thickness gives a weight fraction in the particle rich region of 0.65).
Similar improvements were observed with polyimides (PIXU 218, UP JOHN) but not with polysulfone.

According to reference [2], amino functional silanes are efficient in improving the adhesion of thermosetting and thermoplastic resins to mineral surfaces. The mechanism often assumed or postulated is the formation of an interpenetrating polymer network (IPN) at the mineral surface when no reaction between the amino group of the coupling agent and the polymer chain is possible. The improvement observed in this study might be the result of such a mechanism, i.e. due to the formation of an IPN with the silane coupling agent, the polymer chains remains in contact with the mineral surface upon evaporation of the solvent.
The silane coupling agent Z-6032 (Dow Corning) was used to improve the structure of silicalite-1 filled TPX membranes. However, no significant improvement was observed [10] when the membranes were cast at room temperature despite indications of a good coupling between silane and zeolite (XPS analysis).

Gas permeation

Only a few membranes were tested with respect to their gas separation properties. Furthermore, the results obtained did not confirm the improvement observed by SEM, i.e. the selectivity remained lower than that of the pure polymer and the permeability for CO_2 became higher. Figure 7 gives an example of variation of the separation properties for two PEI membranes filled with A-1100 modified silicalite-1.

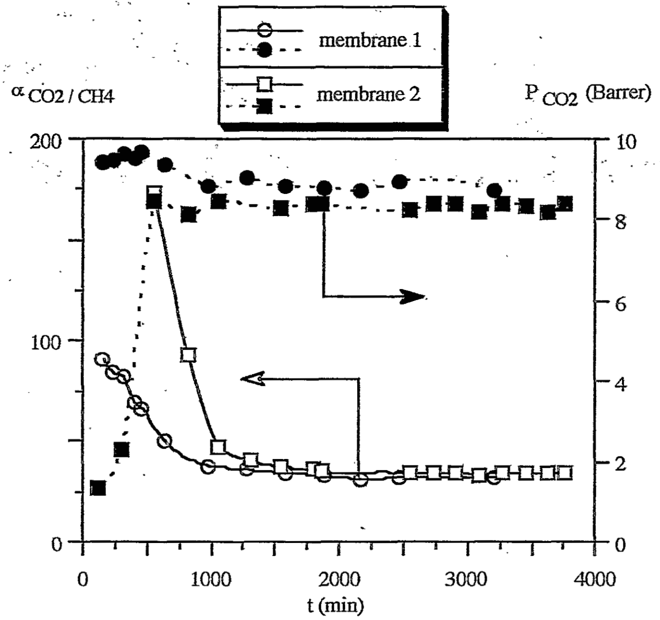


Figure 7: CO_2 permeability and CO_2/CH_4 selectivity of PEI membranes filled with 50wt% of A-1100 modified silicalite-1.

The values for the unmodified silicalite-1 at the same weight fraction are P_{CO_2}=15 Barrer and α_{CO_2/CH_4}=34 at steady state. This means that the modification of the zeolite only resulted in a (slight) decrease of the membrane permeability without affecting the selectivity. The improvement of the internal structure as demonstrated in figure 6 accounts for the decrease in permeability compared to the membrane prepared with unmodified silicalite-1 since less voids can be observed. However, the selectivity remains the same and lower than that of the pure polymer. Three hypothesis can be made:

- the internal structure is still not good enough.
- silicalite-1 cannot improve the selectivity of PEI.
- the silane coupling agent molecules present at the zeolite external surface hinder the diffusion of gas molecules through the zeolite pores.

The last hypothesis is not valid, because if the zeolite pores were blocked by the silane molecules, no increase in permeability would be observed, i.e. the opposite effect is expected. It is more likely that the improved internal structure is not good enough and that the increase of permeability is due to remaining voids. However, the second hypothesis cannot be ruled out since the experimental results suggest, as can be seen from figure 3 a) of chapter III, that silicalite-1 seems less effective to improve the selectivity of an already quite selective polymer (α_{CO_2/CH_4}=17) compared to a poorly selective one. Hence when a polymer is used with a selectivity in the range of 40 to 60, one might expect a relatively small effect of silicalite-1 on the separation properties.

A2.4- Preparation of the membranes above the glass transition temperature

The problems encountered are obviously related to the glassy state of the polymer phase at room temperature. When rubbery polymers are used, no adhesion problems were observed. By solvent evaporation from the zeolite-polymer solution at room temperature, the glass transition is crossed at a given polymer concentration. At this point the polymer chains become much less flexible than in the rubbery state and stress forces are created which might result in dewetting of the polymer from the zeolite external surface.

In the method investigated here the solvent is evaporated above the glass transition temperature of the pure polymer. This implies that the whole process occurs above Tg of the polymer. Polymethylpentene (TPX MX001, Mitsui) with a glass transition temperature of Tg=36 °C as measured by Differential Scanning Calorimetry (Perkin Elmer System 4 with a TADS 3600 data station) was used as polymer.

The membranes were cast from a hot polymer solution (60°C) on a hot glass plate in an oven (60°C) flushed with nitrogen. After evaporation of the solvent, the internal structure was observed by Scanning Electron Microscopy.

Unfortunately, this preparation method did not improve the wetting of the particles by the polymer phase very much, as can be seen from figure 8.

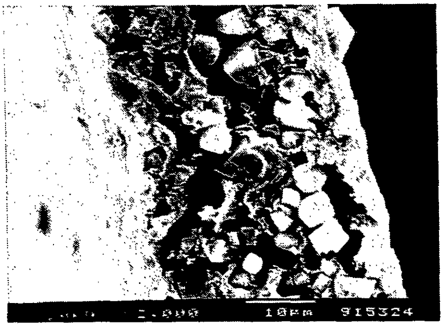


Figure 8: Typical example of the internal structure of a silicalite filled (40 vol%) TPX membrane prepared at 60°C with PCE as solvent (X2000).

The only significant improvement of the structure was observed when the Z-6032 modified zeolite was used (figure 9). However, the non-homogeneous dispersion of the zeolite particles into the polymer matrix (clustering) does not allow to present any gas permeation results, since all the membranes were leaking.

Figure 9: Internal structure of a TPX membrane filled with Z-6032 modified silicalite (30 vol%) prepared at 60 °C with PCE as solvent (X3500).

A2.5- Heat treatment

In this paragraph, heat treatment in a vacuum oven at elevated temperature and also temperature increase under mechanical pressure are considered.

Heat treatment at 150°C

This process was investigated with a PEI membrane filled with zeolite KY (50 wt%). This membrane was placed in a vacuum oven at 150°C for 4 weeks. The gas separation properties were measured again after this treatment. Figure 10 shows the variation of the carbon dioxide permeability and selectivity with time for this membrane.

It can be observed that both the selectivity and the permeability increase with time, which is similar to the results with rubbery polymers which have been reported in chapter V. The selectivity increases from 8 to 52 over a period of about ten days. In the meantime, the carbon dioxide permeability reaches a steady state value after 3 days. This means that a further increase in selectivity is due to a decrease in methane permeability. The steady state CO_2 permeability is 23 Barrer, which is much higher than the pure polymer permeability (1.5 Barrer after heat treatment) but the selectivity is somewhat lower (52 instead of 61).

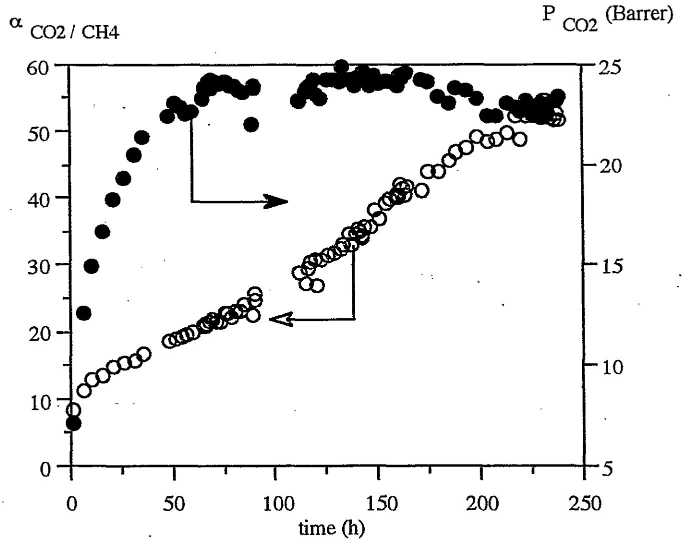


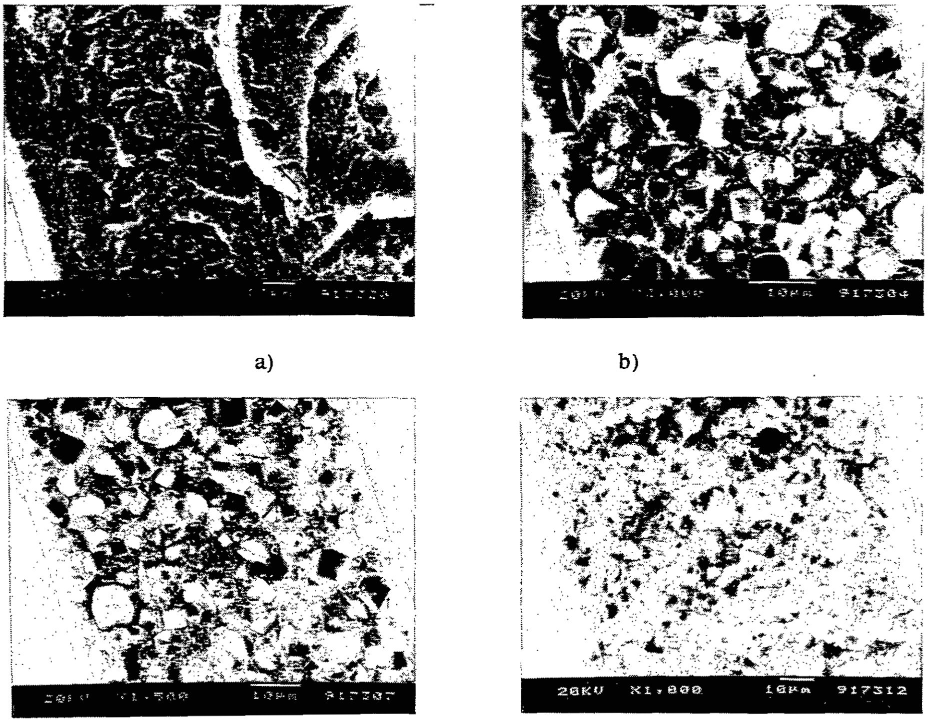
Figure 10: CO_2 permeability and selectivity over CH_4 versus time for a KY filled (50 wt%) PEI membrane annealed at 150°C during 4 weeks.

However, the separation properties of the filled membrane before heating, P_{CO_2}=95 Barrer and α_{CO_2/CH_4}=43, should be taken into account. The heat treatment resulted in a large decrease in permeability and a slight increase in selectivity. This cannot be explained only by a large decrease of the number of voids in the membrane because it could be observed by SEM that still some have remained after the heat treatment. The time dependency of the separation properties in this particular case is not really well understood yet.

Heat treatment with mechanical pressure

In this method, a mechanical press (Lauffer) has been used to combine both mechanical stress and thermal treatment. The membranes were placed between two stainless steel plates, which were in turn placed between two heating plates which can be adjusted to a certain mechanical pressure. TPX was used as polymer because of its relatively low melting temperature of 240°C.

At first polymer pellets were spread on the plates, then a weight of 6 ton was applied on top of the plates and the temperature of the plates was increased up to 240°C. After 10 minutes, the plates were cooled down and the TPX membrane was obtained (see figure 11a).
The same experiment was carried out with solution-prepared silicalite-1 filled TPX membranes and varying the time under pressure and the temperature. Figure 11 (b, c and d) shows some examples of the structures obtained.



a) b)

c) d)

Figure11: Filled and unfilled TPX membrane prepared in the molten state under mechanical pressure: a) pure TPX, 6ton, 240°C, 10 min (x1000); b) TPX + 40vol% silicalite-1, 6ton, 240°C, 10 min (x2000); c) TPX + 30vol% silicalite-1, 6ton, 240°C, 2 min (x1500); d) TPX + silicalite-1 30vol%, 6ton, 240°C, press and cool down (x1000).

All the filled membranes treated in this way were mechanically damaged and no gas separation properties could be determined. Furthermore, the membranes were brown after the treatment, indicating a possible degradation of the polymer phase. This was not expected because pressurizing the pure polymer at 240°C during 30 minutes does not result in any visible polymer degradation. However the presence of silicalite-1 might be the cause of the observed phenomena. Nevertheless, it can be observed that minimizing of exposure time at high pressure and temperature results in a better adhesion polymer-zeolite than in the case of a solution cast membrane, though far from perfect. The same trend was observed with silicalite-1 filled PEI membranes, but also here the membranes were damaged after treatment.

The same experiment was carried out at 250°C with pre-evacuated membranes and under a nitrogen atmosphere. The membranes were placed between two Teflon plates. The result was the same, i.e. brown pieces of membrane. The structure obtained is shown in figure 12.

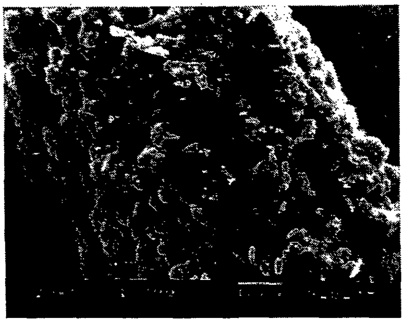


Figure 12: SEM cross-section of a silicalite-1 filled TPX membrane treated at 250°C in nitrogen atmopshere under moderate mechanical pressure (x1500).

However, a significant improvement of the structure can be observed, i.e. much less voids between the zeolite particles and the polymer phase are left. Unfortunately, it was not possible to obtain pieces of membranes large enough to be tested for gas separation.

A2.6- Conclusions

The preparation of a zeolite filled membrane from a glassy polymer by the classic dissolution-casting-evaporation process results in a three phase membrane: zeolite, polymer and voids. This might be due to stress forces occuring during the evaporation step which lead to the dewetting of the polymer chains from the zeolite external surface.
Surface modification of the zeolite particles resulted in a considerable improvement of the internal structure of silicalite filled PEI membranes. However, permeation results could not illustrate this improvement.
Evaporation of the solvent above the glass transition temperature did not give any positive result for the system TPX/silicalite-1.
High temperature treatments did improve the structure but damaged membranes were obtained and polymer degradation occurred.

From these experiments it can be concluded that the most promising approach is the modification of the zeolite's external surface by means of a coupling agent combined with the preparation of the membrane at high temperatures if the problem of polymer degradation can be solved. A possible new method may be the use of a zeolite whose external surface has been covered with a very thin layer of a polymer compatible with the matrix polymer. This thin layer could be grafted by means of silane coupling agent in a first step, and the resulting adsorbent could be incorporated into the desired polymer.
At last, a very elegant way of dealing with this problem might be the direct

polymerization of the matrix polymer around the zeolite particles by a bulk or interfacial polymerization.

Acknowledgement: The authors wish to thank A.Kemperman for his devoted contribution to this investigation.

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[2]- E.P.Pluedemann, *Silane Coupling Agents,* second edition, Plenum Press (1991).
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[5]- E.P.Pluedemann, *Cationic unsaturated amine-functional silane coupling agent,* U.S.Patent 3,819,675 (1974).
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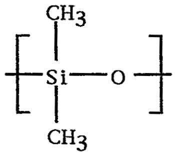
[7]- *Union Carbide Organofunctional Silane A-1100,* product information folder F-41929C 12/80-4M.
[8]- *Dow Corning® Z-6032 Silane (Styryl amine functional silane),* product information folder 23-062C-01 (1985).
[9]- ref.2, chapter 7, p.218.
[10]-A.Kemperman, Master Thesis, University of Twente (1991).

Appendix 3

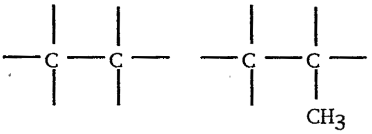
Polymer chemical structures

This appendix shows the chemical stuctures of the polymers used or mentioned in this dissertation.

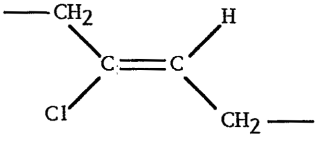
polydimethylsiloxane
(PDMS)



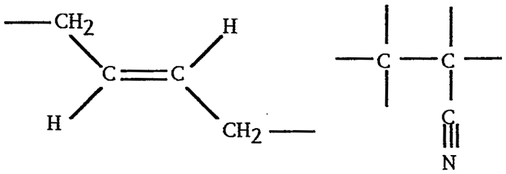
ethene-propene rubber
(EPDM)
(cross-linked for
pervaporation)



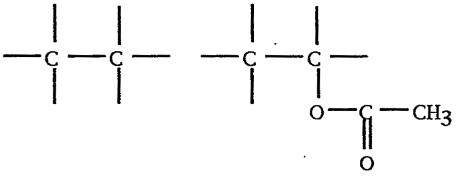
polychloroprene
(PCP)



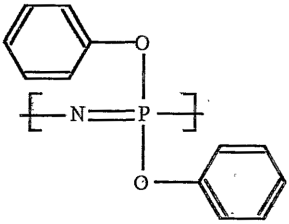
Nitrile Butadiene Rubber
(NBR)
(cross-linked for
pervaporation)



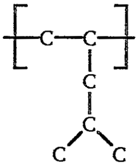
poly(ethylene-vinyl acetate)
(EVA)
(cross-linked for
pervaporation)



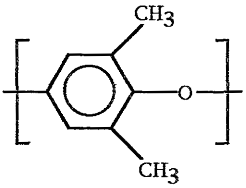
poly(diphenoxy-phosphazene)



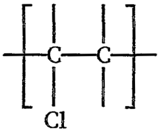
poly (4-methyl-1-pentene)
(TPX)



poly(2,6-dimethyl-1,4-phenylene oxide)
(PPO)

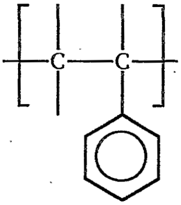


polyvinylchloride
(PVC)

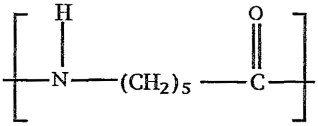


$\left[-\mathrm{C}(\mathrm{Cl})-\mathrm{C}-\right]$

polystyrene
(PS)

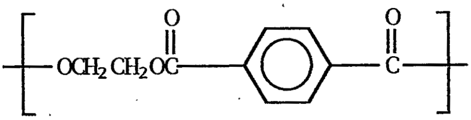


Nylon 6

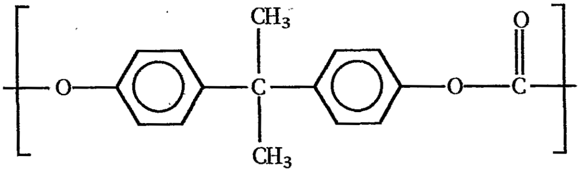


$\left[-\mathrm{N}(\mathrm{H})-(\mathrm{CH_2})_5-\mathrm{C}(=\mathrm{O})-\right]$

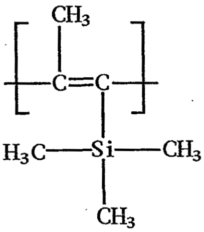
poly(ethylene terephtalate)
(PET)

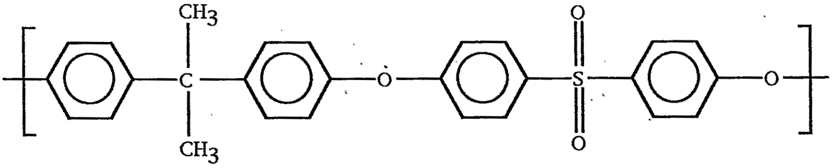


polycarbonate
(PC)



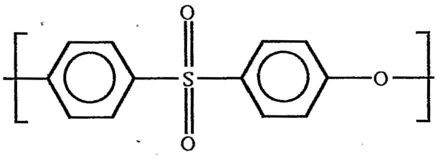
polytrimethylsilylpropyne
(PTMSP)

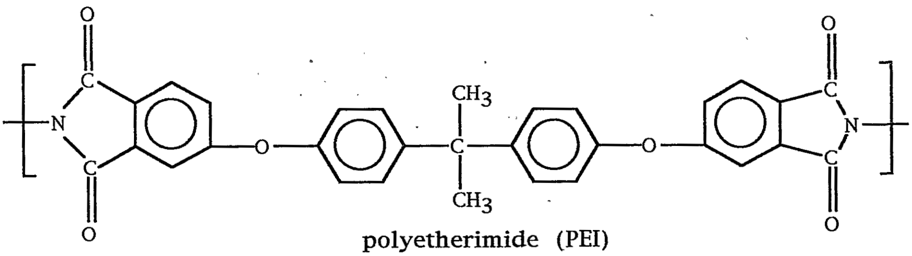




polysulfone (PSF)

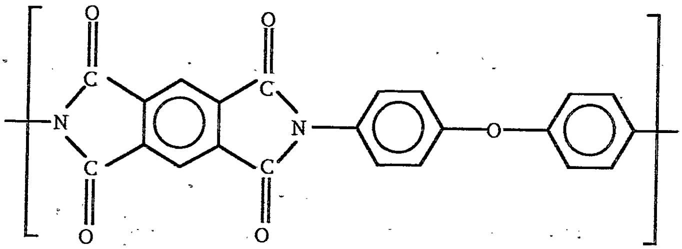
polyethersulfone
(PES)

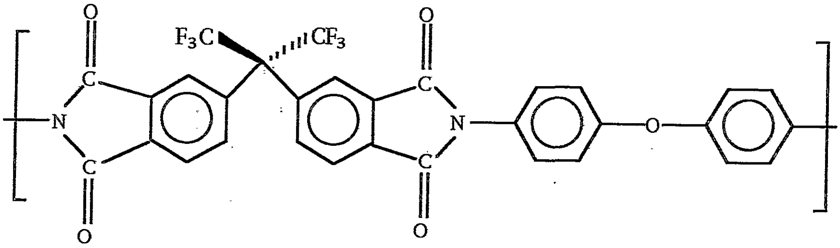




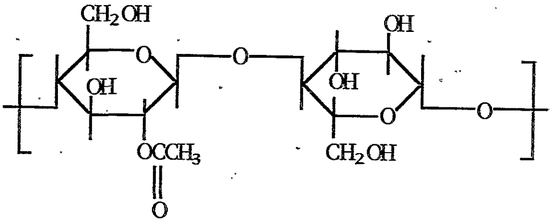
polyetherimide (PEI)

polyimide (PI)
(Kapton)

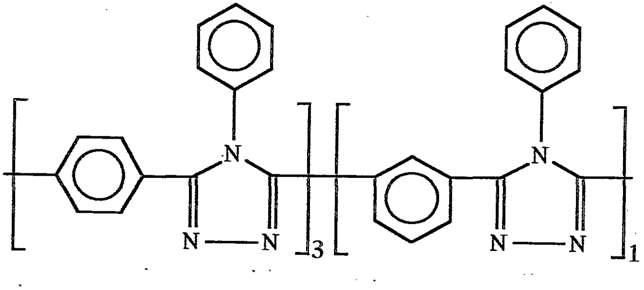




polyimide (6FDA-4,4-ODA)

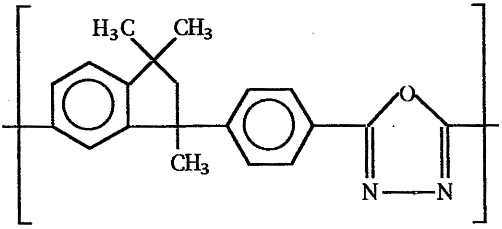


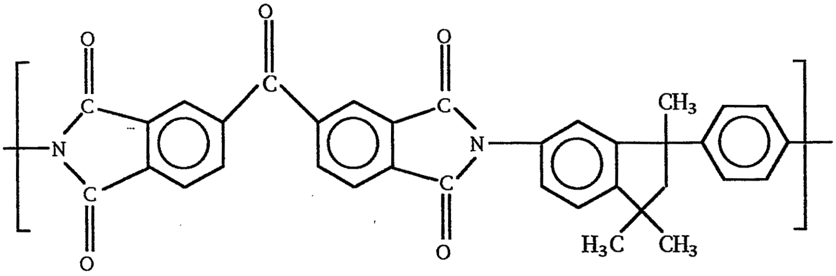
cellulose acetate



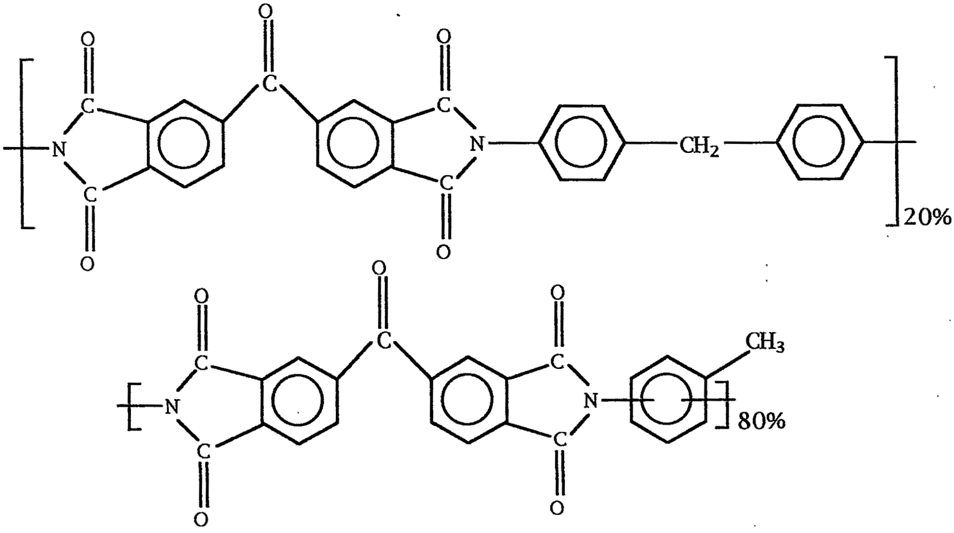
random poly[p-, m-phenylene-(4-phenyl)-1,2,4-triazole]
(PT-75/25)

polyoxadiazole
PIDA-POD





polyimide (PIXU 218)



polyimide (Upjohn 2080)

Summary

Nowadays research in membrane technology aims at improving the efficiency of the separation process to make it more competitive in comparison to conventional separation techniques. The improvement of the membrane material is a way to achieve this goal, especially in the case of pervaporation and gas separation. The incorporation of microporous adsorbents into a polymer material might result in better separation properties. This was shown in the case of silicalite-1 into a silicone rubber matrix used for the pervaporation of alcohol/water mixtures.
Microporous adsorbents like active carbons, molecular sieve carbons and zeolites are conventionally used in batch or semi-continuous processes for separation purposes. Their specific separation properties are due to selective sorption of one species over others or/and to different rates of adsorption (molecular sieving). The present study investigates the use of these materials in continuous membrane processes (gas separation and pervaporation).

In chapter I, a general introduction on membrane based separation processes and adsorbent materials is given, as well as a literature review on the use of adsorbent materials in membrane applications.

In chapter II the pervaporation of a toluene/ethanol mixture by means of active carbon filled polymeric membranes shows that these materials are not suitable for a membrane application due to a non-interconnected porous system. They result in a decrease of the flux and do not influence the selectivity. On the other hand, zeolites like silicalite-1 or dealuminated Y result in a decrease of both toluene flux and selectivity, indicating molecular sieving of the toluene molecules.

In the case of gas separation (chapter III), the application of carbon molecular sieves as adsorbent leads to the same conclusion, i.e. the porous structure of this adsorbent is not suitable for a membrane application. Nevertheless, zeolites like silicalite-1, 13X and KY result in a large improvement of both permeability and selectivity for carbon dioxide over methane when they are incorporated into rubbery polymers. For instance the selectivity for carbon dioxide of EPDM rubber can be increased from 4.3 up to 18 and the permeability from 81 to 395 Barrer by incorporation of zeolite KY. The beneficial effect of silicalite-1 and KY on the selectivity and the permeability for carbon dioxide is observed for a series of rubbery polymers whose selectivities are in the range of 3 to 18 and carbon dioxide permeabilities in the range of 3 to 3000 Barrer. On the other hand, the smaller pore size zeolite 5A does not improve the selectivity of rubbery polymers and lowers the permeability. Silicalite-1 also improves the oxygen/nitrogen separation properties of silicone rubber and EPDM. All these zeolites are responsible for a very large increase of the carbon dioxide sorption capacity of the membrane, but in the case of zeolite 5A the sorbed molecules do

not diffuse through the particles and thus do not participate in the transport.

In chapter IV, the influence of the intrinsic properties of the zeolite on the gas separation properties of the membrane is investigated. The small pore size zeolites (type A) do neither improve the selectivity, nor the permeability for carbon dioxide of highly or poorly permeable rubbery polymers despite their seemingly suitable pore size. Zeolites with a one-dimensional porous structure are also not beneficial. In the case of zeolite Offretite, the improvement of the gas separation properties observed when it is incorporated into EPDM rubber is directly linked to the extent of removal of the organic template used for the synthesis. It indicates that the transport really occurs through the internal porous system of the zeolite. This is also confirmed when studying the effect of changing the cations present in hydrophilic zeolites X and Y. Large and bivalent cations hinder the transport of carbon dioxide resulting in a less important increase of selectivity and permeability than with monovalent cations.

Chapter V concentrates on the transport mechanism through zeolite filled polymeric membranes. Non-steady state permeation shows that in silicalite-1 filled membranes the transport is diffusion controlled whereas with hydrophilic zeolites A, Y and X the sorption plays a major part resulting in a so-called pseudo-sorption controlled transport. This mechanism is explained by the presence of water of hydration in these zeolites which makes the sorption step much slower than in silicalite-1. Activation energies of permeation decrease when zeolites like silicalite-1, KY or 13X are incorporated in EPDM compared to the pure polymer for the series of gases He, CO_2, Ar, O_2, N_2, CH_4. The facilitation factor based on the activation energies indicates that for these three zeolites and the gases investigated, no molecular sieving is observed. Furthermore, the selectivity of zeolite filled membranes for various pairs of gases increases significantly when the temperature decreases. The effect of the feed pressure is only noticeable at low pressures (decrease of the permeability when the feed pressure increases).

Finally, in chapter VI we try to get some more insight in the transport properties of the zeolite. First, permeability models are investigated. They can describe the experimental results very well but the "zeolite permeability" defined is not an intrinsic property of the zeolite since it seems to depend on the polymer phase present around the particles. The dual-mode sorption approach is considered to model the equilibrium sorption isotherms and the kinetics of sorption in zeolite filled polymeric membranes. An activation energy of permeation of carbon dioxide in silicalite-1 is extrapolated from the results obtained with the filled EPDM membranes, tending to prove that diffusion plays the major part in this zeolite. Finally a separation power is defined for EPDM as polymer phase, showing that zeolites KY and Offretite are the best filler in the case of the carbon dioxide/methane separation.

Résumé

Les efforts de recherche dans le domaine des technologies membranaires visent à l'heure actuelle à rendre les procédés utilisant des membranes encore plus compétitifs par rapport aux techniques de séparation conventionnelles. Un des axes de recherche principaux est l'amélioriation des propriétés séparatrices des matériaux employés pour la fabrication de membranes, et ceci plus particuliérement dans le cas de la pervaporation et de la séparation des gaz. L'incorporation d'adsorbants microporeux au sein d'une matrice polymérique est une façon d'y parvenir, comme il a été démontré dans le cas de la pervaporation de mélanges alcools/eau au moyen de membranes en caoutchouc silicone chargées de silicalite-1.
Les adsorbants microporeux tels que les charbons actifs, les tamis moléculaires carbonés et les zéolithes sont dans la plupart des cas utilisés de manière discontinue ou semi-continue dans des procédés de séparation. Leur efficacité dans certains procédés de séparation est la conséquence de l'adsorption sélective d'un composant d'un mélange par rapport aux autres et/ou de différentes cinétiques d'adsorption (tamisage moléculaire). Dans la présente étude, l'emploi de ces propriétés séparatrices en continu au sein d'une membrane est envisagé en pervaporation et séparation des gaz.

Le premier chapitre est une introduction générale sur les procédés de séparation par membranes et les adsorbants microporeux. Une étude bibliographique concernant l'emploi d'adsorbants sous la forme de membrane en continu dans des procédés de séparation constitue la fin de ce chapitre.

La pervaporation d'un mélange organique toluène/éthanol au moyen de membranes chargées de charbons actifs est considérée dans le chapitre II. L'étude démontre que ce type d'adsorbant ne convient pas à l'amélioration des propriétés séparatrices des polymères considérés (sélectifs pour le toluène), ceci étant la conséquence de pores non interconnectés. En fait l'incorporation de charbons actifs résulte en une diminution du flux au travers des membranes et une sélectivité inchangée. Par contre les zéolithes silicalite-1 et Y désaluminée ont pour effet une diminution du flux et de la sélectivité, ce qui indique que les molécules de toluène sont exclues de la structure poreuse de ces zéolithes.

Dans le cas de la séparation des gaz, il est démontré dans le troisième chapitre que les tamis moléculaires carbonés ont eux aussi une structure poreuse dont les pores ne sont pas ou trés peu interconnectés. A l'opposé, des zéolithes telles que silicalite-1, 13X et KY conduisent à une amélioration trés importante de la sélectivité et de la perméabilité pour le dioxide de carbone par rapport au méthane lorsqu'elles sont incorporées au sein d'un caoutchouc EPDM. Par exemple la sélectivité augmente de 4.3 à 18 et la perméabilité de 81 à 395 Barrer par l'incorporation de la zéolithe KY. La silicalite-1 améliore également les

propriétés séparatrices des caoutchoucs silicone et EPDM dans le cas oxygène/azote. Parallèlement la zéolithe 5A qui a un diamètre de pore inférieur ne conduit pas à un accroissement de la sélectivité mais à une diminution de la perméabilité pour le dioxide de carbone par rapport au méthane. Toutes ces zéolithes accroissent de manière importante la sorption du dioxide de carbone au sein des membranes mais dans le cas de la zéolithe 5A les molécules adsorbées ne diffusent pas au travers des particules de zéolithe et ne participent donc pas au transport.

L'influence des propriétés intrinsèques des zéolithes est étudiée dans le chapitre IV. Les zéolithes à pores étroits (type A) n'améliorent ni la sélectivité ni la perméabilité pour le dioxide de carbone de polymères caoutchouteux trés ou trés peu perméables, ceci en dépit d'une taille de pore semblant convenir. Les zéolithes ayant un système poreux mono-dimensionnel, telles que Theta-1 ou Mordenite, sont également inefficaces pour améliorer les propriétés de séparation des gaz de l'élastomère EPDM. La sélectivité et la perméabilité de membranes EPDM chargées de la zéolithe Offretite sont directement liées à la fraction des molécules organiques nécessaires à sa synthèse encore présentes dans les pores de la zéolithe. Ceci indique que le transport des molécules de dioxide de carbone a réellement lieu dans les pores de la zéolithe. L'échange des cations présents dans les zéolithe hydrophiles X et Y montre que la présence d'un cation bivalent (Ca^{++}) ou de taille importante (Ba^{++}) rend la sorption et la diffusion du dioxide de carbone plus difficile et ainsi diminue l'effet de la zéolithe sur la sélectivité et la perméabilité du caoutchouc EPDM par rapport à une zéolithe comportant un cation monovalent (Na^+).

Le chapitre V est destiné à une meilleure compréhension du mécanisme de transport de molécules gazeuses dans les membranes polymériques chargées de zéolithes. La perméation d'un mélange dioxide de carbone/méthane à l'état non-stationnaire montre que le mécanisme de transport dans les membranes chargées de silicalite-1 est controlé par la diffusion. Par contre pour les membranes incorporant des zéolithes hydrophiles telles que 5A, X et Y, le phénomène d'adsorption joue également un rôle important. En fait un accroissement simultané de la sélectivité et de la perméabilité est observé au cours du temps jusqu'à ce que l'état stationnaire soit atteint, ce qui est peu commun dans le domaine des membranes. Le mécanisme de transport est alors pseudo-controlé par l'adsorption. L'explication d'un tel mécanisme est la présence de molécules d'eau au sein de ces zéolithes, ce qui rend l'étape d'adsorption beaucoup plus lente que dans le cas de la silicalite-1. L'énergie d'activation pour la perméation diminue lorsque les zéolithes silicalite-1, 13X et KY sont incorporées dans un caoutchouc EPDM et ceci pour tous les gaz considérés (He, CO_2, Ar, O_2, N_2, CH_4). Ceci indique que pour tous ces gaz le transport est facilité par la présence de la zéolithe, la facilitation décroissant avec le diamètre cinétique du perméant. De plus la sélectivité des membranes chargées de zéolithes pour différentes paires de gaz est largement dépendante de la température de perméation. Enfin, l'influence de la pression d'alimentation est seulement remarquable à basse pression (décroissance de la perméabilité quand la pression augmente).

Finalement, le chapitre VI est consacré à l'étude des propriétés de transport de la zéolithe elle-même. Grâce à des modèles dévelopés pour décrire la perméation au travers de membranes hétérogènes, une perméabilité de la silicalite-1 peut être définie lorsqu'elle est incorporée dans le caoutchouc EPDM. Cependant elle n'est pas une propriété intrinsèque de la zéolithe dans la mesure oú elle n'est pas applicable à la prédiction de la perméabilité d'une membrane chargée de silicalite-1 préparée avec un autre polymère. Le modèle de sorption selon deux modes est employé pour décrire les isothermes de sorption et aussi la cinétique de sorption dans les membranes chargées de zéolithes. A partir des résultats obtenus avec des membranes EPDM chargées de silicalite-1, on extrapole une énergie d'activation de perméation du dioxide de carbone au sein de la silicalite-1, ce qui tend à montrer que dans cette zéolithe la diffusion joue un rôle plus important que l'adsorption. Enfin un pouvoir de séparation est calculé pour les membranes EPDM chargées de différentes zéolithes, montrant que les zéolithes KY et Offretite sont les plus bénéfiques pour l'amélioration des propriétés de séparation dans le cas du mélange dioxide de carbone/méthane.

Zusammenfassung

Die Forschung in der Membrantechnologie ist heute vorwiegend darauf gerichtet, den Wirkungsgrad des Trennprozesses zu erhöhen und dadurch dieses Verfahren gegenüber konventionellen Trennmethoden konkurrenzfähig zu gestalten. Eine Möglichkeit, dieses Ziel zu erreichen, ist die Verbesserung des Membranmaterials. Das gilt vor allem für die Gastrennung und Pervaporation. Die Trennung von Alkohol/Wasser-Mischungen mit Silikongummi Membranen gefüllt mit Silikalit-1 hat gezeigt, daß eine Kombination von mikroporösen Adsorbentien und Polymer zu verbesserten Trennergebnissen führen kann.

Mikroporöse Adsorbentien, wie zum Beispiel (z.B.) Aktivkohle, Molekularsieb-Kohlenstoff und Zeolite, werden für Trennprobleme in dis- und halbkontinuierlichen Prozessen angewendet. Ihre spezifischen Trenneigenschaften basieren auf der selektiven Sorption einer Spezies gegenüber anderen und/oder der unterschiedlichen Sorptionsgeschwindigkeit (Molekularsieb). Die vorliegende Arbeit untersucht die Anwendbarkeit dieser Materialien in kontinuierlichen Prozessen (Gastrennung, Pervaporation).

Kapitel I ist eine allgemeine Einführung in Trennprozesse mittels Membranen. Außerdem wird ein Überblick über physiko-chemische Eigenschaften anorganisch-adsorptiver Materialien gegeben. Der Einbau dieser Adsorbentien in Polymermembranen sowie deren praktische Anwendung werden kurz beschrieben.

In Kapitel II wird am Beispiel der Trennung von Toluen/Ethanol-Mischungen mit Hilfe von mit Aktivkohle gefüllten Polymermembranen gezeigt, daß dieses Material für eine Anwendung in Membranprozessen aufgrund seiner Struktur nicht geeignet ist. Sie führen zu einer Abnahme des Flusses und haben keinen Einfluß auf die Selektivität. Andererseits führen Zeolite wie Silikalit-1 oder dealuminiertes Y sowohl zu einer Abnahme des Flusses als auch der Selektivität, was auf einen Molekularsiebeffekt bezüglich der Toluen-Moleküle hinweist.

Werden Membranen mit Kohlenstoff-Molekularsieben in der Gastrennung eingesetzt (Kapitel III), so erhält man vergleichbare Ergebnisse, das heißt, daß die poröse Struktur dieses adsorptiven Zusatzes nicht für die Anwendung in Membranprozessen geeignet ist. Hingegen führt der Einsatz von Zeoliten wie z.B. Silikalit-1, 13X und KY in Elastomeren zu einer bedeutenden Verbesserung sowohl der Permeabilität als auch der Selektivität für Kohlendioxid gegenüber Methan. So können z.B. für Membranen aus EPDM durch Zusatz des Zeolites KY die Selektivität von 4.3 auf 18 und die Permeabilität von 81 auf 395 Barrer gesteigert werden. Ein positiver Effekt konnte für eine Reihe von Elastomeren, gefüllt mit Silikalit-1 und KY, hinsichtlich der Erhöhung der Selektivität von 3 auf ca. 18 und der Permeabilität von 3 auf ca. 3000 Barrer für Kohlendioxid erzielt werden. Hingegen hat Zeolit 5A, der eine kleine Porengröße besitzt, keinen Einfluß auf die Selektivität von Elastomeren, führt aber zu einer Erniedrigung der Permeabilität. Durch Zusatz von Silikalit-1 zu Silikongummi und EPDM kann ebenfalls eine Verbesserung der Trennergebnisse für Sauerstoff/Stickstoff-Mischungen erreicht werden. In all diesen Fällen zeichnen diese Zeolite verantwortlich für eine sehr bedeutende Erhöhung des Sorptionsvermögens der Membran hinsichtlich des Kohlendioxids, wobei jedoch im Fall des Zeolit 5A die adsorbierten Moleküle nicht durch die Zeolitpartikel diffundieren und somit nicht zum diffusiven Stofftransport beitragen.

In Kapitel IV wird der Einfluß der intrinsischen physiko-chemische Eigenschaften der Zeolite auf die Gastrennungseigenschaften der gesamten Membran untersucht. Zeolite mit kleine Poren (Typ A) beeinflussen weder die Selektivität noch die Permeabilität für Kohlendioxid von Elastomeren mit hoher oder niedriger Permeabilität, trotz ihrer scheinbar günstigen Porengröße. Ebenfalls ungeeignet sind Zeolite mit eindimensional poröser Struktur. Für das System Zeolit Offretite in EPDM steht die beobachtete Verbesserung der Gastrennungseigenschaften in direktem Zusammenhang zum Grad, in dem die für die Zeolitsynthese verwendeten organischen Stoffe entfernt werden. Das ist ein Hinweis darauf, daß der Stofftransport tatsächlich durch das Porensystem der Zeolite erfolgt. Dieses kommt ebenfalls zum Ausdruck, wenn das Verhalten der hydrophilen Zeolite X und Y mit unterschiedlichen Kationen untersucht wird. Zweiwertige und Kationen mit großem Volumen hemmen den Kohlendioxid-Transport, was sich in einer geringeren Erhöhung von Selektivität und Permeabilität im Vergleich zu einwertigen Kationen niederschlägt.

Kapitel V beschreibt den Transportmechanismus in zeolit-gefüllten Membranen. Permeationmessungen außerhalb des Gleichgewichtszustandes zeigen, daß der Stofftransport in mit Silikalit-1 gefüllten Membranen diffusionskontrolliert abläuft. Bei Membranen mit den hydrophilen Zeoliten A, Y und X ist die Adsorption geschwindigkeitsbestimmender Schritt. Der hier zugrunde liegende Mechanismus ist ein sogenannter Pseudo-Adsorptions-Mechanismus. Eine Erklärung für das Auftreten dieses Mechanismus ist die durch Hydratationswasser stark eingeschränkte Adsorption im Vergleich zu Silikalit-1. Für eine Reihe von Gasen, wie zum Beispiel He, CO_2, Ar, O_2, N_2, CH_4 werden die Aktivierungsenergien für die Permeation durch mit Silikalit-1, KY und 13X gefüllte EPDM-Membranen im Vergleich zum reinem Polymer verringert. Der auf den Aktivierungsenergien basierende Beschleunigungsfaktor weist darauf hin, daß für die untersuchten Gase und die drei Zeolite kein Molekularsiebeffekt beobachtet werden konnte.

Weiterhin erhöht sich die Selektivität von Membranen mit adsorptiven Füllstoffen für unterschiedliche Gaspaare, wenn die Temperatur erniedrigt wird. Der Einfluß des Feed-Druckes wird nur bei niedrigen Drücken wahrgenommen (Verringerung der Permeabilität bei Erhöhung des Feed-Druckes), was wahrscheinlich durch eine dabei auftretende Verfestigung der Membranen bedingt ist.

Kapitel VI beschäftigt sich mit dem Stofftransport in den Zeoliten. Veschiedene Modelle zur Beschreibung der Permeabilität werden dabei untersucht. Diese können die experimentellen Resultate sehr gut beschreiben, wobei aber der Modelparameter "Zeolit-Permeabilität" keine intrinsische Eigenschaft der Zeolite ist, sondern von dem sie umgebenden Polymer abhängt. Mit dem "Dual Mode Sorption" Modell können Adsorptionsisothermen sowie die Adsorptionskinetik von zeolitgefüllten Polymermembranen beschrieben werden. Ausgehend von den Ergebnissen der EPDM-Membranen mit Silikalit-1 wurde die Aktivierungsenergie für CO_2 in Silikalit-1 durch Extrapolation erhalten. Diese Werte deuten darauf hin, daß die Diffusion der geschwindigkeitsbestimmende Schritt ist.

Samenvatting

Het onderzoek in de membraantechnologie richt zich tegenwoordig op het verbeteren van de doelmatigheid van het scheidingsproces om deze zodoende beter concurrerend te maken met conventionele scheidingstechnieken. Eén van de manieren om dit te doen is het verbeteren van het membraanmateriaal, vooral in het geval van pervaporatie en gasscheiding. Het toevoegen van microporeuze adsorbentia aan een polymeer zou kunnen leiden tot een verbetering van de scheidingseigenschappen zoals is aangetoond in het geval van silicaliet-1 in een siliconrubber membraan dat gebruikt wordt voor pervaporatie van alcohol/water mengsels.
Microporeuze adsorbentia worden normaliter in batch of semi-continue scheidingprocessen gebruikt. Hun specifieke scheidingseigenschappen zijn een gevolg van de selectieve sorptie van één van de componenten en/of een verschil in sorptiesnelheid (molekulaire zeefwerking). In dit proefschrift wordt het gebruik van dit soort materialen in continue membraanprocessen zoals pervaporatie en gasscheiding besproken.

In hoofdstuk I wordt een algemene inleiding gegeven over membraanprocessen en adsorbentia, evenals een literatuuroverzicht van het gebruik van adsorbentia in membraantoepassingen.

Pervaporatie van een tolueen/ethanol mengsel met behulp van met actief kool gevulde polymere membranen gevuld wordt besproken in hoofdstuk II. Aangetoond wordt dat deze materialen niet geschikt zijn voor membraantoepassingen ten gevolge van het ontbreken van een continue poriestructuur. Ze resulteren in een afname van flux en hebben geen invloed op de selectiviteit. Toevoegen van zeolieten leidt echter tot een afname van zowel flux als selectiviteit, hetgeen duidt op zeefwerking van het zeoliet waarbij transport van tolueen gehinderd wordt.

In het geval van gasscheiding (hoofdstuk III) leidt het gebruik van aktief kool tot een-zelfde conclusie d.w.z. de poreuze structuur van aktief kool is niet geschikt voor membraantoepassingen. Toevoegen van zeolieten zoals silicaliet-1, 13X en KY aan rubberachtige polymeren leidt tot een enorme verbetering van zowel permeabiliteit als selectiviteit voor een mengsel van kooldioxide en methaan. Zo kan door het toevoegen van KY aan EPDM-rubber, de selectiviteit voor kooldioxide worden verhoogd van 4.3 tot 18 terwijl de permeabiliteit toeneemt van 81 tot 395 Barrer. Het positieve effect van silicaliet-1 en KY op de permeabiliteit en selectiviteit voor kooldioxide is waargenomen voor diverse rubberachtige polymeren met een selectiviteit variërend van 3 tot 18 en een permeabiliteit variërend van 3 tot 3000 Barrer. Zeoliet 5A, welke een kleinere poriediameter heeft, verlaagt de permeabiliteit en heeft geen effect op de selectiviteit. Silicaliet-1 leidt ook tot de verbetering van de eigenschappen van silicionrubber en EPDM in het geval van zuurstof/stikstof scheiding. Al deze zeolieten zijn verantwoordelijk voor een grote toename in sorptiecapaciteit van kooldioxide maar in het geval van zeoliet 5A kunnen de gesorbeerde moleculen niet door het zeoliet diffunderen en dragen zodoende niet bij tot het transport.

In hoofdstuk IV wordt de invloed van de intrinsieke eigenschappen van het zeoliet op de gasscheidingseigenschappen van het membraan bestudeerd. Zeolieten met een kleine poriegrootte (type A) leiden niet tot een verbetering van selectiviteit of permeabiliteit van polymeren ondanks hun schijnbaar geschikte poriegrootte. Zeolieten met een één-dimensionaal poriesysteem zijn ook niet gunstig. In het geval van zeoliet offretiet is de mate waarin de gasscheidingseigenschappen worden verbeterd een directe functie van de mate waarin de templateverbinding, die in de synthese wordt gebruikt is verwijderd. Dit duidt er op, dat het transport plaats vindt door het poriesysteem van het zeoliet. Dit wordt bevestigd door het bestuderen van het effect van het kation dat aanwezig is in zeoliet X. Grote en bivalente kationen hinderen het transport van kooldioxide en resulteren in een minder spectaculaire toename van selectiviteit en permeabiliteit dan in het geval van monovalente kationen.

In hoofdstuk V wordt de nadruk gelegd op het transportmechanisme door zeolietgevulde membranen. Non-steady-state permeatiemetingen laten zien dat in het geval van membranen gevuld met silicaliet-1 het transport bepaald wordt door diffusie. In het geval van de hydrofiele zeolieten A, X en Y heeft de sorptie de grootste invloed op het transport en het mechanisme zou als zodanig pseudo-sorptie bepaald genoemd kunnen worden. Dit mechanisme wordt verklaard aan de hand van hydratatiewater dat in zeolieten aanwezig is, waardoor de sorptiestap veel langzamer verloopt dan in het geval van silicaliet-1. Ook is gebleken dat voor de reeks gassen He, CO_2, Ar, O_2, N_2 en CH_4 de activeringsenergieën voor permeatie in EPDM worden verlaagd door het toevoegen van silicaliet-1, KY en 13X. Een "facilitation factor" gebaseerd op deze activeringsenergieën laat zien dat voor de bestudeerde zeolieten en gassen geen moleculair zeefeffect wordt waargenomen. Verder blijkt de selectiviteit van zeolietgevulde membranen significant toe te nemen bij lagere temperaturen. Het effect van de voedingsdruk (lagere permeabiliteit bij hogere voedingsdruk) is alleen waarneembaar bij lage drukken.

In hoofdstuk VI, tot slot, wordt getracht meer inzicht te krijgen in de transporteigenschappen van zeolieten. Eerst worden permeabiliteitsmodellen bestudeerd. Met behulp van deze modellen kunnen de experimentele resultaten goed beschreven worden. De "zeoliet permeabiliteit" geeft echter niet een intrinsieke waarde; deze blijkt een functie van de rond het zeolietdeeltje omliggende polymeerfase te zijn. De "dual-mode sorption" benadering wordt gebruikt om de evenwichtsisothermen en de sorptiekinetiek van zeoliet gevulde membranen te beschrijven. Een waarde voor de activeringsenergie voor CO_2 in silicaliet-1, die is bepaald door extrapolatie van resultaten verkregen met zeolietgevulde EPDM membranen, lijkt aan te tonen dat diffusie de grootste rol in dit zeoliet speelt. Tot slot wordt een "scheidend vermogen" (separation power) gedefinieerd met EPDM als polymeerfase. De verkregen waarde voor het scheidend vermogen laat zien dat de zeolieten KY en Offretiet de beste additieven zijn voor de scheiding van kooldioxide en methaan.

Qui est Jean-Marc ?

Né le 16 Novembre 1967, Jean-Marc a obtenu un baccalauréat série C en 1984 (Institut Notre Dame, Dreux). Suite à ce diplôme, il s'est consacré pendant deux années à la préparation des concours aux Grandes Écoles d'Ingénieur au Lycée Lakanal (Sceaux). Ayant été admis à l'École Nationale Supérieure des Industries Chimiques (ENSIC, Nancy) en 1986, il y a passé trois années à l'issue desquelles il a obtenu le diplôme d'ingénieur ENSIC et également un Diplôme d'Études Approfondies en Génie des Procédés (Institut National Polytechnique de Lorraine) en 1989. En Octobre 1989 il a incorporé le groupe Technologies Membranaires (professeur Smolders, puis Strathmann) de la Faculté de Chimie de l'Université de Twente (Pays-Bas) en tant que Volontaire du Service National, puis en tant qu'étudiant en thèse, le projet de recherche étant financé par le Groupement de Recherches de Lacq (Elf Aquitaine, France). En Avril 1993, il intégrera la Société Michelin (Clermont Ferrand, France).

Who is Jean-Marc ?

Jean-Marc was born on November 16, 1967 at Dreux (Eure et Loir, France). He got the Baccalauréat C in 1984 and then joined the preparatory classes in the Lakanal highschool in Sceaux to prepare the "concours d'entrée aux Grandes Écoles d'Ingénieur". In October 1986, he started studying in Nancy at the "École Nationale Supérieure des Industries Chimiques" where three years later he obtained the "Ingénieur" degree and a "Diplôme d'Études Approfondies" in Process Engineering. Since October 1989 he has been working in the membrane technology group (professor Smolders, then Strathmann) of the Chemical Technology Department at the University of Twente (Netherlands). In April 1993, he will join the Michelin company (Clermont Ferrand, France).

Wie is Jean-Marc ?

Jean-Marc is geboren op 16 November 1967 in Dreux (Eure et Loir, Frankrijk). In 1984 kreeg hij het Baccalauréat C (Institut Notre-Dame, Dreux) en ging vervolgens naar het Lycée Lakanal (Sceaux) om zich voor te bereiden op de "concours d'entrée aux Grandes Écoles d'Ingénieur". In oktober 1986 begon hij zijn studie aan "École Nationale Supérieure des Industries Chimiques" in Nancy, waar hij na drie jaar zijn Ingenieurs diploma en een "Diplôme d'Études Approfondies" in Chemische Technologie behaalde. In oktober 1989 begon hij met zijn promotie onderzoek in de groep Membraantechnologie (professor Smolders en later Strathmann) aan de Universiteit Twente (Nederland). Per April 1993 zal hij in dienst treden van Michelin (Clermont Ferrand, Frankrijk).