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DEVELOPMENT AND CHARACTERISATION OF POLYANILINE-BASED COMPOSITE MEMBRANES FOR GAS-SEPARATION

Dissertation
GERHARD ILLING
May 2002

Loughborough University, Loughborough
ABSTRACT

Polyaniline-based membranes were developed during this work. The combination of polyaniline with PVDF offers the opportunity of creating large, dense and stable membrane areas in a simple and reproducible way.

New production techniques were tested to meet the requirements of large scale applications and to overcome the poor mechanical properties of polyaniline. In order to fulfil industrial requirements, with PVDF a material was found that combines well with polyaniline and forms stable and thin composite membranes having high flux and selectivity in gas-separation applications.

By simultaneous reduction of the film thickness the permeation rate could be increased by at least 5 times compared to the data in other publications. The thickness of the polyaniline layer could be reduced down to 1.6 µm. The separation factors for some interesting gas pairs are: \( \text{H}_2/\text{CO}_2 (3.5) \), \( \text{CO}_2/\text{CH}_4 (40) \) and \( \text{O}_2/\text{N}_2 (7) \).

In the case of nitrogen, diffusion coefficients were determined that are by some orders higher than those observed by other authors.

Also the impact of factors such as the exchange state, membrane thickness, temperature and feed pressure on selectivity and permeability were tested.

Thinnest polyaniline layers on PVDF supports allowed the observation of permeation change during doping and dedoping the membranes. It has also been illustrated in how far the gas flux responds to doping. In these tests the change of permeability was observed in situ.

Smallest microporous defects can be plugged without affecting the polyaniline layer itself, and still maintaining selectivity. The combination of polyaniline / PVDF with siloxanes allows plugging microscopic defects without restricting the permeant flux.

In sorption tests in the case of oxygen, the Dual-mode model was found to be appropriate to describe sorption, whereas sorption on nitrogen could satisfactorily be described by the Langmuir isotherm.

Isotherms of carbon dioxide indicate that the Dual-mode model applies at pressures up to 35 bar. Multi-layer sorption and condensation at still higher pressures can be described by the BET model.

Keywords: Polyaniline, Composites, Membranes, Gas-Separation, Sorption, Diffusion, Permeability, Selectivity
ACKNOWLEDGEMENTS

This work was carried out at Loughborough University, Department of Chemical Engineering, and the University of Applied Sciences in Emden / Germany.

There are a number of people whose assistance and contributions have made this dissertation possible.

Special thanks go to my 1st supervisor, Dr. Klaus Hellgardt, who supported this work a lot with his precious instruction, guidance and interest. His great enthusiasm and knowledge was a constant source of inspiration.

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I would also like to acknowledge the donation of Dr. Berhard Wessling, the managing director of ORMECON, Germany, and the financial support during the course of this work. The financial contributions allowed me to concentrate on the research.

Some of my student colleagues who worked in the same scientific field gave me some inspiration and lots of helpful discussions. Especially, Morten Schonert helped me much with some creative ideas and experimental assistance.

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Also Klaus-Peter Fried, Dr. Cristine Dauelsberg, Dr. Kai Fischer, Dr. Sven Hagemann, Arnold Terviel, and Johannes Diekhoff contributed much to the work carried out in Germany.
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1 Introduction

In 1991, Anderson et al.\(^3\) published results for selectivities of various gas pairs permeating through polyaniline films. Selectivity values for these gas pairs surpassed the highest previously reported values for other highly selective membranes.

Highest selectivities were achieved by doping, dedoping and controlled redoping of this polymer. Doping significantly alters the gas transport properties of the polymer. A reversible doping process allows doping with different agents. Thus controlled modification of the membrane morphology can be achieved in order to separate a particular gas pair.

The aim of the present work is to assess the applicability of polyaniline membranes for gas separation applications and finding methods to modify polyaniline membranes and to enhance basic properties such as permeability and selectivity.

Commercial scale production of polyaniline dispersion by ORMECON provides a reproducible source of the polymer. New production techniques are needed to meet the requirements of large scale applications, and comparative research is required to gain deeper insights into the separation process itself.

In order to determine the selectivity of polyaniline for various gases, suitable testing devices have to be developed. Methods have to be found to produce polyaniline membranes in a reproducible way and to overcome the poor mechanical properties of the polymer. The influence of the exchange state of the membrane is of great importance for mechanical properties and separation performance.

Furthermore, the impact of factors other than the exchange state, e.g. membrane thickness, temperature and feed pressure on selectivity and permeability must be taken into consideration to assess separation qualities. In order to fulfil industrial requirements, materials have to be found to produce stable, thin composite membranes having high flux and selectivity. Sorption qualities have to be investigated and models need to be developed to predict membrane performances. All these issues are addressed in the present work.

Polyaniline (Figure I-1) is a dopable, conjugated polymer similar to polypyrrole, polythiophene or poly(p-phenylene). Polyaniline can exist in various oxidation states characterised by the ratio of amine to imine nitrogen atoms\(^1\). In order to create polyaniline, aniline monomers are polymerised by an oxidative polymerisation reaction to a polysemiquinone radical cation salt. The conducting form of polyaniline is associated with intermediate oxidation states, and features an equal number of imine and amine nitrogens. In base form (emeraldine base) polyaniline is an insulator.
The conductive salt form is obtained upon treatment with acids. Introducing anions into the polymer (doping) allows a change from the insulator state ($< 10^{-10}$ S/cm) to electric conductivity ($> 1$ S/cm).

Polymers that conduct electricity without being blended with conducting inorganic materials are called "intrinsic conducting polymers" (ICP). Their specific properties are founded in the polyanionic structure and morphology. By inserting or removing anions with different properties and shape the pore connectivity within the polymer structure can be tailored\(^2\). Charge transport within the polymer films can be modified by changing the morphology of the films\(^4\) or blending polyaniline with other high performance polymers\(^5\).

Based on the conductivity and specific properties of polyaniline a number of applications have been investigated: rechargeable batteries\(^6\), blends and composites with common polymers for use in antistatic coatings, electromagnetic shielding and microwave adsorption have been pro-
duced. Moreover, chemical sensors, corrosion prevention of metals, catalysts, electrochromic devices and light emitting diodes using polyaniline have also been demonstrated.

Starting in the late 80's, polyaniline membranes for gas separation applications have been studied by a number of groups.

The introduction of gas separation membranes for industrial applications occurred almost three decades ago. Although membrane-based gas separation is a quite new separation technique, it is one of the most significant new processes that have appeared in the past thirty years. Membranes are used for various separation tasks such as the separation of gas mixtures, dehydration of solvents, separation of dissolved ions, separation of organic solvents etc.

Membrane technology for the separation of liquid-liquid and liquid-solid streams has been practised in the industry for many years (e.g. reverse osmosis, ultrafiltration, microfiltration and other membrane-based processes). Advances in membrane technology in these other areas gradually led to the development of membranes suitable for industrial gas separations. Gas separation by membranes competes with cryogenic and a variety of adsorption and absorption processes (e.g. pressure swing adsorption, amine treatment, iron sponge, etc.).

The mechanism of many gas separation membranes is based on solution-diffusion. The key membrane performance variables are selectivity, permeability and durability. For solution-diffusion membranes, permeability is defined as the product of the solubility and diffusivity. One major drawback is the lack of membranes yielding high flux and high selectivity. High selectivity membranes have lower permeability and vice versa; membranes with high selectivity and permeability are not yet available for many gas separation applications.

For a wide variety of industrial applications the separation of mixtures of gases is essential and there is a continuously increasing interest in membrane-based gas separation as an energy efficient alternative to other separation processes, e.g. air separation, removal of CO2 and H2S from flue gas, extraction or recovery of H2 from purge gases, recovery from hydrocarbon refinery processes or the adjustment of the syngas ratio.

Gas separation is often practised with well established technologies such as cryogenic distillation, adsorption, and chemical separation. The choice of purification techniques depends on the requirements for gas purity and the amount, source and application of the gases have to be considered. For many processes and applications, gas purities of 99.9% are quite sufficient.

Exemplary for cost estimation, Figure 1-2 (adapted from Prasad et al.) shows the cost-effectiveness comparison of various nitrogen separation systems. On the y-axis the nitrogen purity can be seen and the x-axis shows the corresponding volume flow per hour (MCFH = ...)
Million Cubic Feet per Hour. The individual areas indicate the most cost effective solution under the respective boundary conditions of purity and volume flow.

![Diagram](image)

Figure 1-2: Cost-effectiveness comparison of gas separation processes

Direct economic comparison of the different separation technologies is difficult because of incomplete statistical data\(^ {13} \). Nonetheless, membrane separation systems offer specific advantages such as low energy consumption, ease of operation, reduced space requirements, and also modular construction.

With the development of gas separation membranes, a solution has been found that is highly competitive with existing processes. Membrane-based gas separation must compete primarily on the basis of cost effectiveness and convenience. The advantages that membrane technology offers are represented by a rapidly growing investment of the industry in membrane-based gas separation technology. While the annual sale of membranes and membrane-related products was about 0.5 billion US$ in 1985, it rose to 2.9 billion US$ in 1996\(^ {26} \) and up to 5 billion US$ in 1998\(^ {27} \), and is still rising annually by 5-15%.

Polyaniline-based composite membranes that have been developed during this work are promising materials to achieve the desired high selectivity. It was possible to increase flux rates by up to 100 times over existing polyaniline membranes.
Theoretical background

New production techniques even allow the production of switchable membranes in a quite simple and reproducible way. This work was supported by ORMECON CHEMIE (Ammersbek / Germany), one of the first companies world-wide to develop methods to produce and to process polyaniline on a large scale.

This thesis is divided into four main parts. The directory on page 6 presents the main structure of the four parts. A more detailed directory can be found at the beginning of each individual part.
2 Theoretical background

2.1 Permeation through porous and non-porous membranes

2.1.1 Gas transport in polymeric materials

Permeation of gases through polymers is considered to be a transport process. The molecules of a gas pass a membrane because of their physical properties, the driving forces, and the mobility of the permeant. The amount of molecules that have crossed the material is expressed as $J$, the flow rate. The gas flux across the membrane is defined as

$$ J_i = \frac{Q_i}{A_M \cdot t \cdot p_i} \quad [I-1] $$

with

- $J_i$: flux of compound $i$ (cm³/cm² bar s)
- $Q_i$: gas volume (cm³)
- $A_M$: membrane area (cm²)
- $t$: time (s)
- $p_i$: pressure (bar).

This term gives information on the gas volume $Q$ that passes a certain area $A$ at pressure $p_i$ within a given time $t$. The permeability can be calculated at steady state conditions if the gas flux is constant. With known pressure difference $\Delta p$ across the membrane and thickness $\ell$ of the material, the permeability coefficient can be applied to define transport rates.

$$ P = \frac{Q \cdot \ell}{A \cdot t \cdot \Delta p} \quad [I-2] $$

The permeability is expressed as $P$ according to SI-units under STP (standard temperature and pressure, 253.15K and 101325Pa) conditions:

- $P$: permeability \( (\text{cm}^3 \text{STP} \cdot \text{cm})/\text{cm}^2 \cdot \text{s} \cdot \text{Pa} \)
- $\ell$: membrane thickness (cm)
- $\Delta p$: pressure difference between feed and downstream side (Pa)

If the thickness of the membrane cannot be determined or if the permeation only depends on a thin selective layer in a multi-compound material, the corresponding expression for the flow rate will be
Theoretical background

The flux of molecule $i$ under STP-conditions is given by 

$$J_{n,i} = \text{flux of molecule } i \text{ under STP-conditions} \left( \frac{\text{cm}^3\text{STP}}{\text{cm}^2 \cdot \text{s} \cdot \text{Pa}} \right).$$

Commonly in the Anglo American literature the permeability coefficient $P_i$ is expressed as Barrer:

$$1 \text{ Barrer} = 10^{-10} \frac{\text{cm}^3\text{STP} \cdot \text{cm polymer}}{\text{cm}^2 \text{polymer} \cdot \text{s} \cdot \text{cmHg}}$$

By multiplication with the factor $7.4 \cdot 10^{-4}$, the expression Barrer can be converted into SI units:

$$1 \text{ Barrer} = 7.4 \cdot 10^{-4} \frac{\text{cm}^3\text{STP} \cdot \text{cm polymer}}{\text{cm}^2 \text{polymer} \cdot \text{s} \cdot \text{Pa}}.$$ 

The selectivity of a membrane is generally expressed as separation factor. In the case of permeation into vacuum ($p_2 \approx 0 \text{ bar}$), the separation factor only depends on the quotient of the permeabilities of the individual gases and is expressed as

$$\alpha^{id}_{A/B} = \frac{P_A}{P_B}$$

where

$\alpha^{id}_{A/B}$ ideal separation factor

$P_A, P_B$ permeabilities of gases A and B

The following models for gas transport represent calculations for idealised conditions, the corresponding main separation mechanisms are presented in Figure I-3. In reality, two or more of the described mechanisms take place at the same time. Simultaneous occurrence of various different mechanisms at the same time means that in reality the total flux is a sum of those transport processes.

2.1.2 Gas transport by viscous flow

For theoretical considerations, the transport in porous materials is mathematically approximated by a model that is based on flux through parallel and cylindrical pores. The equations for viscous flow and Knudsen diffusion are valid for individual gases and do not regard interactions between the gas molecules and the membrane material.
Theoretical background

The mechanism of permeation in such a pore structure mainly depends on the ratio of mean free path $\lambda_M$ of the gas molecules to the pore diameter $d_p$ and is determined by the Knudsen number $^{28}$:

$$K_n = \frac{\lambda_M}{d_p}$$

Viscous flow occurs when pores in the membrane material are large relative to the mean free path of the gas (about 100 to 200nm at 1bar and 293K)$^{29}$. In this case the molecules within the pore interact much more with each other than they interact with the pore walls.

In the simplest case for $d_p \gg \lambda_M$ and $K_n \ll 1$, the flow can be described by Poisouille’s Law$^{30}$:

$$J_n = \frac{r_p^4 \cdot \pi \cdot (p_1^2 - p_2^2)}{16 \ell_p \cdot \eta \cdot p_n}$$

where

- $J_n$ volume flux (related to the membrane area) (cm$^3_{STP}$/cm$^2$)
- $r_p$ pore radius (cm)
- $\ell_p$ pore length (cm)
- $p_n$ pressure during determination of the gas flux (bar)
- $p_1$ pressure on upstream side (bar)
- $p_2$ pressure in downstream volume (bar)
- $\eta$ dynamic viscosity (Pa·s)

A more substantial view of the occurring forces can be expressed by the Hagen-Poiseuille Law for Newtonian fluids and gases. The relation between molecules that pass the pores and the effective pressure difference in the pores is also considered and results in the following expression which describes the flux$^{31}$:

$$J_n = \frac{r_p^2 \cdot \overline{p} \cdot T \cdot A_p}{128 \cdot \ell \cdot \eta \cdot T} \cdot \frac{T_n}{p_*} \cdot (p_1 - p_2)$$

with

- $\overline{p}$ mean pressure within pore (Pa)
- $\eta$ mean dynamic viscosity (Pa·s)
- $T$ temperature (K)
- $A_p$ pore area (cm$^2$)
Theoretical background

<table>
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<tr>
<th>Figure 1-3: Gas transport mechanisms of gases in porous and non-porous membranes with $D_p = \text{diameter of pore, } D_G = \text{diameter of gas molecule}</th>
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<tr>
<td>Feed</td>
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<td>$D_p &gt;&gt; D_G$</td>
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| Feed | Knudsen Diffusion |
| $D_p > D_G$ | $K_n \sim 1$ |
| $K_n > 1$ |
| Separation based on the inverse square root of molecular weights of permeants |

| Feed | Molecular sieving (surface diffusion) |
| $D_p \geq D_G$ | $K_n \gg 1$ |
| Separation by size exclusion and penetrant-surface interactions |

| Feed | Solution-diffusion |
| Separation by gas-membrane interactions, solubility, and mobility of the molecules between the polymer chains. Transport through opening transient gaps. |
2.1.3 Transport by Knudsen diffusion

Regarding Knudsen diffusion two sub-mechanisms can be distinguished:

a) range \( d_p \sim \lambda_M, (K_n \sim 1) \)

If the gas mean free path is in the range of the pore diameter, the transport mechanism is described as "slip flow" and can be formulated as

\[
J_n = \frac{\pi \cdot r_p^2 \cdot (p_1 - p_2)}{M \cdot \bar{v} \cdot \ell \cdot 2} \tag{1-7}
\]

where

- \( M \) molecular mass (g/mol)
- \( \bar{v} \) mean velocity of gas molecules (m/s).

b) range \( d_p > \lambda_M, (K_n > 1) \)

In case the pore diameter is significantly larger than the mean free path (i.e. in mesopores with a pore diameter of 2 to 50nm) the interaction of the pore walls with the gas molecules exceeds the interaction of the molecules with each other. In this system the gas has access with the low pressure side via a small hole. The number of gas molecules that pass through the hole is equal to that of molecules "colliding" with the area \( A_0 \) of the hole. Consequently the number of molecules that pass through the hole will be

\[
Z \cdot A_0 = \frac{p \cdot A_0}{\sqrt{(2 \cdot \pi \cdot m \cdot k \cdot T)}} \tag{1-8}
\]

where

- \( Z \) collision frequency (1/s m³)
- \( A_0 \) collision area (cm²)
- \( k \) Boltzmann constant \( 1.38066 \cdot 10^{-23} \) (J/K)

From this process follows Graham's Law and it can be expressed with the following equations and finally the ideal separation factor \( \alpha \) can be derived.

From the relations

\[
\frac{\Delta p}{\Delta t} \propto \frac{\Delta N}{\Delta t} \propto Z \cdot A_0 \tag{1-9}
\]

and

\[
M_r = \frac{m}{m_u} \tag{1-10}
\]

with
Theoretical background

\[ M_r \] relative molecular mass (kg)

\[ m \] mass (kg)

\[ m_u \] atomic mass unit 1.6606 \cdot 10^{-27} (kg)

the result for \( \alpha \) is:

\[
\alpha^k_{B,A} = \frac{\frac{\Delta N_A}{\Delta t}}{\frac{\Delta N_B}{\Delta t}} = \frac{\frac{p \cdot A_p}{\sqrt{(2 \cdot \pi \cdot m_A \cdot k \cdot T)}}}{\frac{p \cdot A_p}{\sqrt{(2 \cdot \pi \cdot m_B \cdot k \cdot T)}}} = \sqrt{\frac{m_B}{m_A}} = \sqrt{\frac{M_B}{M_A}} \]  \[ I-11 \]

with

\[ \alpha^k_{B/A} \] ideal separation factor for Knudsen diffusion

\[ \Delta N_{A,B} \] difference of amount of molecules A, B (mol)

\[ \Delta t \] time interval (s)

\[ T \] temperature (K)

\[ A_p \] pore area (cm²)

\[ p \] pressure (Pa)

\[ k \] Boltzmann constant 1.38066 \cdot 10^{-23} (J/K)

\[ M_{A,B} \] molecular mass of molecules A and B (g/mol).

It follows that the separation factor for two gases in the regime of Knudsen diffusion is based on the inverse square root ratio of the molecular weights of the two gases.

Each molecule maintains its mass-dependent velocity and Knudsen flow occurs. From kinetic gas theory Knudsen also derived a formula to express the volume flow of individual components,

\[
J_{n,i} = \frac{8}{3} \sqrt{\frac{R}{2 \cdot \pi \cdot T \cdot M_i}} \cdot \frac{r_p}{\ell_p} \cdot \frac{T_0 \cdot A_p}{p_0} \cdot \Delta p_i \]  \[ I-12 \]

where the index \( i \) is representative for the single compound,

\[ J_{n,i} \] flux of compound i under STP-conditions (cm³_{STP} /cm² Pa s)

\[ R \] universal gas constant (J/mol K)

\[ T_0 \] temperature under STP conditions 273.15 (K)

\[ p_0 \] pressure under STP conditions 101325 (Pa).

The transport of each compound is proportional to \( \Delta p_i \), the driving force between the upstream and the downstream side, in accordance to the viscous flow. The transport of each individual compound, however, depends additionally on the molecular weight \( M_i \).
2.1.4 Transport in microporous membranes

Microporous molecular sieving (using pore diameters of up to 2nm) separation is primarily based on the much higher diffusion rates of the smallest molecule, so that size exclusion can be achieved.

Nevertheless, sorption level differences may also be important factors especially for similarly sized penetrants (e.g. O₂ and N₂).

The transport of gases through these membranes depends on their structure. The transport of gases through microporous membranes can be described as a combination of Knudsen diffusion combined with a flux along the pore walls (surface diffusion). In this case the total gas flux is the sum of surface diffusion and pore flux:

\[ J_t = J_p + J_s \]  \[\text{[I-13]}\]

with

- \( J_p \) pore flux (Knudsen flux) \((\text{cm}^3/\text{cm}^2 \text{ Pa s})\)
- \( J_s \) surface flux \((\text{cm}^3/\text{cm}^2 \text{ Pa s})\)
- \( J_t \) total flux within \((\text{cm}^3/\text{cm}^2 \text{ Pa s})\)

Assuming equilibrium between the gas phase in the pores and the sorbed phase at the pore walls, the gas flow can be described with the following equation by introducing the cross sectional area:\n
\[ J_s = -A_p \cdot D_{sf} \cdot G_p \frac{dc_s}{dl} \]  \[\text{[I-14]}\]

where

- \( A_p \) pore area (cross section) \((\text{cm}^2)\)
- \( c_s \) surface concentration of sorbed gas \((\text{cm}^3_{\text{STP}}/\text{cm}^3)\)
- \( G_p \) geometric factor for pores \((-\cdot\)\)
- \( D_{sf} \) surface diffusion coefficient \((\text{cm}^2/\text{s})\)

The introduction of geometric factors of the pores plays an important role in describing this kind of diffusion.

2.1.5 Models based on free volume in polymers

Free volume in general is a measure of the internal space available in a polymer for the movement of the polymer chain, which has an impact on mechanical properties (i.e. flexi-
Theoretical background

The total "amount" of free volume in the polymer directly depends on the state of the polymer: above the glass transition temperature the free volume significantly increases.

Free volume can arise from motion of the main chain, chain ends, or the side chains. These motions depend on various kinds of structural conformations such as the number of end groups, the length of the side chains, or steric aspects and intermolecular attraction.

Free volume can be increased by the introduction of compounds (and their concentration) which have influence on the above properties. Furthermore raising the temperature has a direct impact on free volume (see also 2.2.1).

Fujita et al.\textsuperscript{34} created a model in which the diffusion coefficient is related to the free volume in polymers. The basic idea is that a molecule can only move from one position to another if there is sufficient empty space.

For gases the molecules of which are much smaller than the monomer units of the polymer, the thermal energy induced mobility of a few monomer units provides enough space for gas molecules to diffuse. This mechanism is driven by the thermal energy of the gas and applies to helium, hydrogen, oxygen, nitrogen and carbon dioxide.

In this model the diffusion coefficient $D_T$ can be related to the free volume $v_f$ as follows:

$$D_T = R \cdot T \cdot A_f \cdot \exp\left(\frac{-B}{v_f}\right)$$

where $A_f$ and $B$ are characteristic parameters: $A_f$ depends on the size and shape of the polymer, while $B$ is related to the minimum free local volume that is required for a displacement.

2.1.6 Diffusion

As a result of thermal activation and movements of surrounding polymer chain segments a permeate dissolved in a polymer will move in random directions. When a concentration gradient is applied to this system, the molecules will be driven along this gradient through the polymer. The transfer of matter by diffusion can be expressed as proportional to the negative gradient of concentration at any point or plane in the diffusion medium with a proportionality coefficient $D$.

The most common mode of gas transport through dense, isotropic membrane media can be expressed by Fick's 1st law where $D$ is defined as the diffusion coefficient,
Theoretical background

\[ J_i = -D_i \frac{\partial c_i}{\partial \ell} \]  

[I-16]

\( J_i \) is the flux-per-unit area of species \( i \) and \( \partial c_i / \partial \ell \) is the concentration gradient.

In such a case the concentration profile is stationary, that means independent of time and location in a way that no concentration-polarisation occurs. Additionally \( D \) is considered to be independent of \( c \).

Fick’s second law of diffusion describes the non steady state, that means the change of concentration with time.

\[ \frac{\partial c}{\partial t} = D \cdot \left( \frac{\partial^2 c_i}{\partial x^2} + \frac{\partial^2 c_i}{\partial y^2} + \frac{\partial^2 c_i}{\partial z^2} \right) \]  

[I-17]

Under circumstances in which diffusion is limited to the x-direction and a diffusion coefficient is independent of the concentration, it simplifies to

\[ \frac{\partial c}{\partial t} = D \cdot \left( \frac{\partial^2 c_i}{\partial x^2} \right) \]  

[I-18]

These equations adequately describe the mass transport and the time dependence of concentration of permanent gases in polymers above the glass transition temperature \( T_g \).

Condensable gases, however, show a concentration dependence of the diffusion coefficient which then becomes a function of concentration, \( D = f(c) \).
2.1.6.1 Experimental determination of the diffusion coefficient

In a typical permeation test the polymer is subjected to the feed pressure on the upstream side with static vacuum maintained downstream. Initially the system is free of permeant. At time zero gas at pressure $p_f$ is applied to the membrane.

At the beginning of permeation the concentration is $c_f = c_\infty > 0$ on the feed side, whereas on the downstream side the concentration is $c_d = 0$. In the course of the permeation process, between non-steady state and steady-state diffusion, the concentration gradient in the membrane will change. With these boundary conditions and $D = constant$, the solution of Fick's second law is

$$Q = \frac{D \cdot c_f}{\ell} \cdot \left( t - \frac{\ell^2}{6D} \right)$$ [I-20]

This term has an intercept on the time axis commonly known as time lag $\tau$. With the relation

$$D_{app} = \frac{\ell^2}{6 \cdot \tau}$$ [I-21]

The apparent diffusion coefficient $D_{app}$ can directly be determined by the time lag method. Without knowledge of the concentration on the membrane surface, the time lag method offers a convenient way to determine the diffusion coefficient at steady state diffusion (cf. Figure I-4).

If the gas pressures are $p_f$ and $p_2$ and the concentrations in the film surfaces are $c_f$ and $c_2$ then the integrated form of Fick's 1st law (eq. I-16) will be

$$J_f = -\frac{D \cdot (c_{i,2} - c_{i,1})}{\ell}$$ [I-22]
Assuming that Henry's law (cf. eq. I-38) applies, eq. I-22 becomes eq. I-29 that describes permeation through a film at steady state. The diffusion coefficient at steady state slope and the permeability can be determined by the use of the time lag method. As the permeability equals $D \cdot S$, also the solubility $S$ can be calculated (cf. eq. I-31).

For polymer temperatures below $T_g$ the diffusion coefficient is considered to be dependent on the concentration of the permeating species. An integral expression for the diffusion coefficient can be derived if the concentration on the downstream side is regarded as negligible ($c \sim 0$):

$$
\bar{D}(c_\infty) = D_{\text{mean}}(c_\infty) = \frac{1}{c_\infty} \int_0^{c_\infty} D(c) dc
$$

[I-23]

The mean diffusion coefficient $D_{\text{mean}}(c_\infty)$ is defined as the mean value of the two diffusion coefficients related to the surface concentrations.

Nonetheless it can be shown that the errors are small if the determination of $D_{\text{mean}}(c_\infty)$ is calculated from the term for the concentration independent diffusion coefficient $^3$, $D$ (eq. I-).
Theoretical background

2.2 Permeation through dense polyaniline films

Gas transport across dense polymers (essentially pore free) can be considered as a process comprising five successive steps:

- Adsorption onto the membrane (feed-side)
- Dissolution in the membrane
- Diffusion of the dissolved gas through the membrane matrix
- Disengagement from the membrane matrix
- Desorption from the permeate-side of the membrane

Gas diffusion through those membranes can be described by the solution-diffusion model based on work that was carried out by Graham\(^36\). Solution-diffusion separation is based on solubility and mobility factors\(^14\). Selectivities based on diffusion favour small molecules whilst selectivities based on solubility favour the most condensable ones. In this model, gas dissolves in the dense membrane material and diffuses through the membrane along a concentration gradient.

If the concentration \(c_i\) of gaseous component \(i\) at the surface of the polymeric membrane is sufficiently small, the equilibrium between the partial pressure of this compound in the vapour phase \(p_i\) is related to the concentration of sorbed gas in the polymer membrane \(c_i\) by Henry’s Law (cf. eq. I-37). Finally a concentration profile can be established across the film if the two surfaces are maintained at different partial pressures as schematically illustrated in Figure I-5.

The transport mechanism in such kind of non-porous membranes is then governed by a combination of Fick’s 1\(^{st}\) law (eq. I-16) and Henry’s law (eq. I-26):

\[
J_i = -D_S \frac{\partial c_i}{\partial \ell} = \frac{D_S \cdot (c_{i,1} - c_{i,2}) \cdot A_M}{\ell} = \frac{Q_t}{A_M} \tag{I-24}
\]

where

- \(A_M\) membrane area (cm\(^2\))
- \(Q_t\) gas volume at time \(t\) (cm\(^3\))

using the relation

\[
S_i = \frac{1}{H_c} \tag{I-25}
\]

with

- \(S_i\) solubility of molecule \(i\) (cm\(^3\)\(_{\text{STP}}\)/cm\(^3\) bar)
- \(H_c\) Henry coefficient (cm\(^3\) bar/cm\(^3\)\(_{\text{STP}}\))
Henry's Law (cf. eq. I-38) can be expressed as:

\[ c_i = S_i \cdot p_i \]  \hspace{1cm} [I-26]

Having established a concentration profile across the membrane thickness \( \ell \) Fick's 1st law of diffusion can be applied to describe the diffusive flux of the component through the membrane, where \( D_S \) is the diffusivity of species \( i \) in the polymer and \( Q_t \) is the volumetric flow rate of species \( i \) permeating through a membrane surface area \( A_M \). The substitution of above equations gives:

\[ Q_t = \frac{P \cdot (p_{i,1} - p_{i,2})}{A_M \cdot \ell} \]  \hspace{1cm} [I-27]

and finally

\[ P = \frac{J \cdot \ell}{(p_{i,1} - p_{i,2})} \]  \hspace{1cm} [I-28]

where \( P \) is the permeability \( p_{i,1} \) is the feed side pressure and \( p_{i,2} \) is the permeate side pressure. Introducing the ideal gas law finally leads to the equation for calculating the permeability of gases through a membrane.

\[ P = \frac{dp}{dt} \cdot V_A \cdot T_0 \cdot t}{(p_1 - p_2) \cdot A \cdot p_0 \cdot T_A} \]  \hspace{1cm} [I-29]

with

\[ \frac{dp}{dt} = \Phi \]  \hspace{1cm} slope at steady state of \( p - t \) transient (Pa/s)
\[ T_A \]  \hspace{1cm} downstream temperature (K)
\[ V_A \]  \hspace{1cm} downstream volume (cm³)
\[ T_0 \]  \hspace{1cm} temperature under STP conditions 273.15 (K)
\[ p_0 \]  \hspace{1cm} pressure under STP conditions 101325 (Pa).

A corresponding expression that describes solution-diffusion can be derived by combining the Henry term (related to the solubility) and the diffusion coefficient (related to diffusivity).
Theoretical background

The permeability of a gas then is a function of the solubility of the gas in the membrane matrix and the diffusivity of the gas through the material. In this case the expression is a product of the two physical effects that determine the transport of gases through polymers:

\[
J_i = P_i = -D_S \frac{\partial c_i}{\partial \ell} = -D_S \cdot S \frac{\partial p_i}{\partial \ell} = \frac{D_S \cdot (p_{i,1} - p_{i,2})}{\ell} \quad [I-30]
\]

or

Permeability \( P \) = Solubility \( S \) \cdot Diffusivity \( D \). \quad [I-31]

![Schematic diagram of transport mechanism of solution-diffusion type membranes](image)

Figure I-5: Schematic diagram of transport mechanism of solution-diffusion type membranes

The main assumptions of the solution-diffusion model are:

- solution is according to Henry’s law.
- diffusion occurs along a concentration gradient in an isotropic membrane matrix.
- ideal transport process; the diffusion coefficient is independent of the concentration and the sorption coefficient is independent of the pressure.
- the sorption processes are much faster than transport by diffusion.
- the flux through the membrane is directly proportional to the applied pressure difference and inversely proportional to the membrane thickness.
- ideally, the solution-diffusion model can only be applied for polymers above their glass temperatures\(^{37}\).
Theoretical background

2.2.1 Temperature dependence of permeation

In general polymer permeability is a function of various factors:
\[ P = f(c, T, \text{chain mobility, crystallinity, cross-linking, polarity, gas-polymer interactions, permeant shape, and others...}) \].

Besides the concentration, the temperature is a major factor which affects polymer chain movement. An increase in temperature provides energy for an increase in segmental motion. Depending on the temperature range the polymer may pass through structural or phase transitions, like the glass and melting transitions, which affect solution and diffusion. The effects of an increase in temperature may also be expressed in terms of an increase in free volume, which is related to the bulk expansion of the polymer due to the increased segmental motions. All this causes an increase in diffusion rates. Penetrants also become less condensable as the temperature rises. As a result, permeability is increasing whereas selectivity decreases.

If the solution process is ideal, with no volume change on mixing, the change in free volume with increasing concentration will be proportional to that obtained by an increase in temperature. Transport through dense films may be considered as an activated process which can usually be represented by an Arrhenius type of equation:

\[
S = S_0 \cdot \exp\left[ -\frac{\Delta H_S}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) \right] \tag{I-32}
\]

and

\[
D = D_0 \cdot \exp\left[ -\frac{\Delta E_D}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) \right] \tag{I-33}
\]

with

- \( \Delta H_S \) solution enthalpy (J/mol)
- \( \Delta E_D \) energy for diffusion (J/mol)
- \( D_0 \) diffusion coefficient at STP (cm²/s)
- \( R \) gas constant (J/mol K)
- \( T_0 \) temperature at STP (K)

From these equations and the premise of the ideal solution-diffusion model, the temperature related equation for permeability can be derived: the permeability of the gas molecules depends on the sum of quantities of the activation energy for diffusion and solution.
Theoretical background

\[ P = P_0 \cdot \exp \left[ \frac{-(\Delta E_D + \Delta H_S)}{R \cdot T} \right] \]  

\[ P_0 \] permeability under STP conditions \( \text{cm}^3_{\text{STP}}/\text{cm}^2 \text{ Pa s} \)

With the relation

\[ E_p = (\Delta E_D + \Delta H_S) \]  

in which \( E_p \) is the activation energy for permeation (J/mol) follows an Arrhenius type expression for permeability:

\[ P = P_0 \cdot \exp \left[ \frac{-(\Delta E_p)}{R \cdot T} \right] \]

2.2.2 Concentration dependence of permeation

Motion of polymer chain segments are affected by two major dimensions: temperature \( T \), and the concentration \( c \) of sorbed penetrant within the polymer. This motions may also be a function of factors such as film thickness \( \ell \), pressure \( p \) and time \( t \).

The presence of sorbed penetrant increases the free volume in the polymer matrix. The concentration dependence differs from the temperature dependence due to the probability of various modes of sorption as adsorption, absorption, incorporation into microvoids, cluster formation, and other modes of mixing.

With the equation \( P = D \cdot S \), the permeability coefficient is defined and either \( D \) or \( S \) or both will vary with \( c, p, \ell \) or \( t \). As a result the permeability coefficient \( P \) is also dependent on those variables. It must be considered that in common penetrant-polymer systems the diffusion coefficient is not a constant but rather a function of the penetrant concentration, \( D = f(c) \), and in some systems of spatial coordinates and/or the lapsed time since diffusion has started.

The concentration dependence is a consequence of the plasticising effect of a sorbed penetrant and/or various mechanisms which localise or immobilise a certain portion of a sorbed penetrant. The spatial and time dependencies are ascribed to structural relaxations on a time scale equal to or greater than that of the diffusion process (e.g. ageing of the membrane).
Permeation of gases with a critical temperature $T_c$ lower than or equal to the process temperature depends only slightly on the pressure difference. E.g. Stern et al.\textsuperscript{39} showed that the permeation of permanent gases like helium and nitrogen through polyethylene was constant over the pressure range from 5bar up to 60bar. In contrast to this observation, for the gases carbon dioxide, ethane, ethene, and nitrogen dioxide an exponential dependence was found between the applied pressure and the permeability.

Permeation tests on cellulose acetate membranes with methane and carbon dioxide showed that the solubility of carbon dioxide in cellulose acetate is five to six times higher than that of methane\textsuperscript{40}. It was also found for this material in another publication of Stern et al.\textsuperscript{41} that the higher permeation rate of carbon dioxide through this material compared to that of methane, nitrogen and helium significantly depends on the system pressure.

### 2.2.3 Concentration polarisation

Concentration polarisation occurs in all membrane processes. When a molecular mixture is applied to a membrane surface, some components permeate the membrane whereas others are retained. In pressure driven processes (i.e. ultrafiltration or reverse osmosis) this leads to accumulation of retained material and at the same time to depletion of the permeating components in the boundary layer close to the membrane surface. The consequences in general are reduced transport and separation qualities.

This effect can be described by the introduction of the mass transfer coefficient, $k_i$ (m/s), where

\[
k_i = \frac{D_i}{\delta}
\]

with

- $D_i$: diffusion coefficient of species in the boundary layer (m$^2$/s)
- $\delta$: thickness of the boundary layer (m)

In membrane systems where the permeation of molecules through the membrane is fast compared to the transport across the boundary layer (e.g. solution-diffusion membranes) the concentration of the permeating species decreases with approaching the membrane. This effect is named boundary layer resistance. In gas separation, this additional transport limiting factor is can be neglected, because the flux is low and the mass transfer coefficient through the boundary is high.
Corresponding concentration profiles can be found e.g. in pervaporation, electrodialysis or gas separation.

Table I-1 compares diffusion coefficients of gases in various media. Representative for other gas mixtures, the diffusion coefficients of hydrogen in oxygen and nitrogen are several magnitudes higher than those of diffusion in other media. For this fact, concentration polarisation in gas separation only plays a minor role.

Table I-1: Diffusion coefficients for various gases in different media

<table>
<thead>
<tr>
<th>Diffusion of gases in media</th>
<th>Hydrogen in oxygen and nitrogen$^{42}$</th>
<th>Hydrogen in $\text{H}<em>2\text{O}</em>{\text{lq}}$$^{43}$</th>
<th>Hydrogen and nitrogen in PVC$^{43}$</th>
<th>Nitrogen in polyaniline$^{44}$ (doped / redoped)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Range of diffusion coefficient (cm$^2$/s)</td>
<td>0.6 / 0.7</td>
<td>$5 \times 10^{-5}$</td>
<td>$4 \times 10^{-7} / 3 \times 10^{-9}$</td>
<td>$2.7 \times 10^{11} / 4.9 \times 10^{10}$</td>
</tr>
</tbody>
</table>
2.3 Sorption on polymers

The gas sorption process in polymers refers to the equilibrium amount of penetrant sorbed and the sorption mode. Sorption in a polymeric matrix can generally be described as the penetration and distribution of the penetrant molecules over two (or more) phases to include adsorption, absorption, incorporation into microcavities between polymeric chains or on preferential sites, cluster formation and other modes of mixing. The distribution of molecules over different modes of sorption may be influenced by changes in temperature, sorbed concentration, swelling-induced structural states, time of sorption to equilibrium and other factors.

If ideal solution behaviour occurs, Henry's law is obeyed: the concentration of the sorbed penetrant is sufficiently small and the penetrant is uniformly dispersed within the polymer. The equilibrium between the partial pressure of the gas in the gas phase and the concentration within the membrane is described by Henry's law\(^{13}\) (cf. Figure I-6):

\[ p_i = H_c \cdot c_i \]  \[\text{[I-38]}\]

where

- \(p_i\): partial pressure of component \(i\) (bar)
- \(c_i\): concentration in the membrane phase (g/cm\(^3\))
- \(H_c\): Henry coefficient (cm\(^3\) bar/cm\(^3\)\(\text{STR}\))

At temperatures above the glass transition temperature, the solubility coefficient then is a constant, independent of sorbed concentration at a given temperature and the sorption isotherm is a linear relation of concentration versus pressure. Provided the gas pressure does not exceed approximately one bar, ideal solution behaviour is observed when permanent gases are sorbed by polymers. Due to small polymer-penetrant interactions and negligible gas-gas interactions, the solubility of permanent gases in polymers is very small (< 0.2% by volume)\(^{45}\). However, in these systems the function is influenced by the relation \(T/ T_c\), where \(T_c\) is the critical temperature of the gas.

With \(T > T_c\) (permanent gases, e.g. H\(_2\), N\(_2\), O\(_2\)) the solution process is described by Henry's Law and the sorption isotherm is linear. At small concentrations the behaviour of more condensable gases at \(T \sim T_c\) or \(T < T_c\) can be described with eq. I-39\(^{46}\):

\[ c_i = [S_0 \cdot \exp(\alpha \cdot c)] \cdot p_i \]  \[\text{[I-39]}\]
Theoretical background

where

\[ \alpha_c \quad \text{constant for concentration dependence} \]
\[ S_0 \quad \text{solubility coefficient at STP conditions} \quad (\text{cm}^3_{\text{STP}}/\text{cm}^2 \text{ bar}) \]

This isotherm is valid for small concentrations and deviates from the linear shape. Nevertheless, others (Paul et al.\textsuperscript{47}) found exact conformity with Henry's law for CO\textsubscript{2} in polymers at temperatures above \( T_g \).

2.3.1 Sorption isotherms

The Figures I-6 to I-9 of isotherms are based on the BET classification of isotherms\textsuperscript{48}.

Ideal solution behaviour is observed and isotherms that result are similar to isotherms as shown in Figure I-6. In this case the penetrant is randomly dispersed within the polymer in a way that Henry’s law can be applied.

![Figure I-6: Henry’s law; slope = constant](image)

Three other general types of sorption isotherms found for sorption by polymers are illustrated in Figures I-7 to I-9.

In physical terms, type I isotherms represent initial sorption on some kind of specific sites in the polymer as expressed according to Langmuir. These isotherms represent a preference for polymer-penetrant pairs to be found at relatively small pressures with a smaller amount of sorption of nearly ideal-solution behaviour at higher pressures. When the sites are nearly all occupied, a small amount of penetrant dissolves in the polymer with a more or less random distribution. This sorption mode is exemplified by the sorption of some ionic polymers, dyes, or polymers containing polar groups.
Theoretical background

Type II isotherms also result when gases are sorbed at high pressures by glassy polymers containing voids. Two modes of sorption have been considered to be involved\textsuperscript{49}: true solution plus sorption into pre-existing voids.

Two modes of sorption have been considered to be involved\textsuperscript{49}: true solution plus sorption into pre-existing voids.

Type III isotherms (cf. Figure 1-8) represent a preference for penetrant-penetrant pairs to be formed such that the solubility coefficient increases continuously with pressure. Such systems can be described by Flory-Huggins\textsuperscript{50} thermodynamics. There are two principal physical interpretations of this behaviour. One is that the first molecules sorbed tend to loosen the polymer structure at some places and make it easier for subsequent molecules to enter in the neighbourhood sites in the beginning and then to diffuse elsewhere.

This interpretation implies that the sorbed penetrant plasticises the polymer. Such isotherms are observed when a liquid or vapour penetrant is a strong solvent or swelling agent for the polymer. Although polymer-penetrant interactions are relatively strong, they are not specific in the sense of site penetrant interactions.

Another physical interpretation of type III behaviour is given in systems in which penetrant-penetrant interactions are stronger than penetrant-polymer interactions.

An example is that of water in comparatively hydrophobic polymers (e.g. polyacrylmetacrylates)\textsuperscript{51}. In this system water is associated through hydrogen bonding in the liquid state and association of clustering of water inside a polymer has to be considered to occur.

It must be expected that stable clusters or aggregates of sorbed penetrant molecules will be less mobile in comparison with isolated molecules. From this it can be concluded that, if the proportion of clustered molecules increases with increasing sorbed concentration $c$ as implied by a type III isotherm, that the diffusion coefficient $D$ of the polymer-penetrant system will decrease with increasing concentration $c$. 

---

Figure I-7: Langmuir equation
Theoretical background

This has been observed in a number of water-polymer systems and contrasts with the behaviour of sorbed solvents or swelling agents when the diffusion coefficient increases with increasing concentration\(^52\).

Type IV isotherms (cf. Figure I-9) may be considered as a combination of type I at low pressures and type III at higher pressures. Such isotherms frequently describe the sorption of water by the more hydrophilic polymers such as wool, silk and cellulosic materials\(^50\), and refer to the BET equation, with site saturation at point B.

Initially (water) molecules are strongly sorbed on sites corresponding to the polar groups (usually hydroxyl, carboxyl or amide) in the polymer. Point B indicates the stage at which monolayer coverage is complete and multilayer adsorption about to begin. At higher relative sorbant (water) pressure solution, or clustering processes predominate.

Nevertheless, it is likely that two or more modes of sorption will occur concurrently.
2.3.2 Dual-mode model

The Dual-mode sorption model\(^{53}\) has been developed in order to describe more complex solution processes of gases in various glassy polymers. This model assumes that the penetrant gas molecules dissolved in the polymer can be distinguished in two thermodynamically distinct populations:

The first population is dissolved following a Henry-type dissolution (cf. Figure I-6) mechanism. The concentration of the molecules \(c_D\) (the index "D" stands for dissolved) is related to the penetrant equilibrium pressure \(p_i\) by a linear isotherm (cf. eq. I-38). From equation 41 follows the corresponding expression for the solubility coefficient \(S_i\):

\[
\text{Henry term: } c_D = S_i \cdot p_i \tag{I-40}
\]

\[
\text{Langmuir term: } c_H = \frac{c_H' \cdot b' \cdot p_i}{1 + b' \cdot p_i} \tag{I-41}
\]

\[
\text{Dual-mode sorption: } c_T = c_D + c_H = S_i \cdot p_i + \frac{c_H' \cdot b' \cdot p_i}{1 + b' \cdot p_i} \tag{I-42}
\]

where

- \(c_D\) concentration dissolved (Henry) (cm\(^3\)STP/cm\(^3\))
- \(c_H\) concentration in holes (Langmuir) (cm\(^3\)STP/cm\(^3\))
- \(c_T\) total concentration (cm\(^3\)STP/cm\(^3\))
- \(b'\) microvoid affinity constant (1/bar)
- \(c_H'\) max. capacity of Langmuir distribution (cm\(^3\)STP/cm\(^3\))

If type V (cf. Figure I-10) isotherms appear, the overall penetrant concentration \(c_T\) will correspond to the sum of Henry and Langmuir concentrations, where \(b'\) represents the affinity constant, the ratio of rate constants of gas adsorption and desorption in microcavities.

The microcavities result from Brownian movements in the polymer and of its side chains. Below glass transition temperature \(T_g\) the mobility of the polymer and its side chains is substantially restricted. On increasing the temperature above glass temperature, the thermal energy is sufficient to overcome the restrictions in polymer movements and the free volume is increasing. Those free sites are filled successively with gas molecules. At low partial pressures, the sum of Henry and Langmuir modes contributes to sorption. With rising pressure, the concentration-versus-pressure isotherm gets linear because the dissolution of gas molecules obeys Henry’s Law.
Theoretical background

Figure I-10: Dual-mode model

The higher the pressure rises, the more explicit is the linearity of the resulting curve. The pressure-dependent solubility coefficient \( S_i \) can be calculated (cf. eq. I-43) by introducing equations I-40 and I-41 into the sorption isotherms \( c_T = f(p) \), and the coefficients \( c_H' \) (the saturation constant of the Langmuir term) and \( S_i \) are thus determined.

\[
\frac{c_T}{p} = S_i + \frac{C_{H',b'}}{1 + b \cdot p} = f(p)
\]  
[I-43]
2.3.2.1 Determination of coefficients $S_i$, $c_H$, $c_H'$ and $b'$

The coefficients for the Dual-mode model can be calculated successively in three steps. This requires the use of mathematical calculation and graphical linearisation as presented in the following:

1. Graphic determination of solubility coefficient $S_i$:

$$\frac{cm^3_{STP}}{cm^3_{polymer}}$$

$$\Delta y \quad \Delta x$$

$$m = S_i \; \text{slope of the linear part}$$

2. Calculation of coefficient $c_H$ and the equation to determine $c_H'$ and $b'$:

$$c_H = c_T - S \cdot p \quad \text{[I-44]}$$

$$c_H = \frac{c_H \cdot b' \cdot p}{1 + b' \cdot p} \quad \text{[I-45]}$$

$$\frac{1}{c_H} = \frac{1}{c_H' \cdot b'} + \frac{1}{c_H'} \quad \text{[I-46]}$$

$$\frac{p}{c_H} = \frac{1}{c_H' \cdot b'} + \frac{p}{c_H'} \quad \text{[I-47]}$$

3. Graphic determination of coefficients $C_H'$ and $b'$:

$$\frac{p}{c_H} = \frac{1}{c_H' \cdot b'} + \frac{p}{c_H'} \quad \text{[I-48]}$$
2.3.3 Dual-mobility model

In the case of diffusion through polymers in their glassy states, the assumption of a concentration independent diffusion coefficient is not valid. Glassy polymers differ in gas transport characteristics: their restricted chain mobility does not allow fast obtaining of equal distribution of the permeant. The Dual-mobility model was developed by Paul et al.\textsuperscript{54} on the basis of the Dual-mode sorption model to describe permeability below the glass transition temperature.

In this model different modes of sorption are related to different mobility terms. The molecules dissolved according to the Henry mode are mobile without restrictions, whereas the molecules in the Langmuir micro-cavities are only partially mobile. Provided that the transport in both modes occurs at the same time and the transport modes do not interact, the permeant flux, in analogy to Fick's first law, is proportional to the sum of the concentration gradients of the modes:

\[ J = -D_D \frac{\partial c_D}{\partial x} - D_H \frac{\partial c_H}{\partial x} \]  \hspace{1cm} [I-49]

where \( D_D \) is the diffusion coefficient of the Henry fraction and \( D_H \) the diffusion coefficient of the Langmuir fraction.

On the premise that the permeant flux is proportional to a concentration independent diffusion coefficient \( D_D \) (a diffusion coefficient that is responsible for the transport of the molecules dissolved according to the Henry mode), the permeability can be expressed as a function of the ratio of the immobilised fraction \( F \):

\[ F = \frac{D_H}{D_D} \]  \hspace{1cm} [I-50]

The permeability becomes:

\[ P = S_i \cdot D_s \cdot \left( 1 + \frac{F \cdot K}{1 + b \cdot p} \right) \]  \hspace{1cm} [I-51]

with

\[ K = \frac{c_H \cdot b}{S} \]  \hspace{1cm} [I-52]

The ratio of the diffusive mobility is expressed as \( F \), the quotient of the diffusion coefficients for the Langmuir (\(-D_H\)) and the Henry (\(-D_D\)) term. Furthermore, the relative amount of the gas
Theoretical background

molecules dissolved (according to the two mechanisms) is expressed by \( K \). If the product \( b \cdot p \) is small, the portion of the Henry fraction is expressed as

\[
D_D = D_{\text{eff}} \cdot \left( \frac{1 + K}{1 + F \cdot K} \right)
\]

where \( D_{\text{eff}} \) is the effective diffusion coefficient that is determined in the time lag experiment. It can be seen that the ratio of the diffusion coefficients directly affects the effective diffusion coefficient. With rising pressure the Langmuir sites are filled successively and now the more mobile molecules of the Henry sites contribute to the total diffusion.

2.3.3.1 Determination of the coefficients \( D_S \) and \( K \)

Also the Dual-mobility equation (I-51) has a graphical solution that enables calculation of the unknown coefficients. A linearisation of this model is given by plotting the permeability over the expression \( \frac{1}{1 + b \cdot p} \).

The equation for the graphic determination of the coefficients can simply be derived by converting eq. I-51 into a suitable form:

\[
P = S_i \cdot D_S + \frac{S_i \cdot D_S \cdot F \cdot K}{1 + b \cdot p}
\]

The intersection of the resulting curve with the y-axis enables the calculation of \( D_S \). With known \( D_S \) from the slope, the last unknown variable \( F \) can be calculated.

\[
b = S_i \cdot D_S
\]

\[
m = F \cdot K \cdot S_i \cdot D_S
\]

\[
\frac{1}{1 + b \cdot p}
\]
2.4 Polyaniline-based membranes

2.4.1 Conductive polymers

Polymers that are electrically conductive without addition of conducting substances are called "intrinsic conducting polymers" (ICP) or "organic metals". Some members of this polymer group are e.g. polypyrrole, polyacetylene, polythiophene or polyaniline. The chemical structure of some selected materials is presented in Table I-2:

Table I-2: Chemical structure of selected intrinsic conducting polymers

<table>
<thead>
<tr>
<th>Material</th>
<th>Chemical Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly-1,4 phenylene sulphide</td>
<td>![Poly-1,4 phenylene sulphide structure]</td>
</tr>
<tr>
<td>Poly-1,4 phenylene vinylene</td>
<td>![Poly-1,4 phenylene vinylene structure]</td>
</tr>
<tr>
<td>Polypyrrole</td>
<td>![Polypyrrole structure]</td>
</tr>
<tr>
<td>Polyvinylene-1,3,4 oxadizole</td>
<td>![Polyvinylene-1,3,4 oxadizole structure]</td>
</tr>
<tr>
<td>Polyacetylene, cis and trans configuration</td>
<td>![Polyacetylene cis and trans configuration structure]</td>
</tr>
<tr>
<td>Polythiophene</td>
<td>![Polythiophene structure]</td>
</tr>
<tr>
<td>Emeraldine base</td>
<td>![Emeraldine base structure]</td>
</tr>
</tbody>
</table>
Theoretical background

The science of conductive polymers is rather young. In 1977, Alan Heeger, Alan MacDiarmid and Hideki Shirakawa discovered that chemical doping of polyacetylene with iodine increases electric conductivity by several orders of magnitude. In general, electrically conductive polymers are composed of conjugated polymer chains with \( \pi \)-electrons that are delocalised along the carbon-carbon, the carbon-nitrogen or the carbon-sulphur backbone. The undoped (neutral) form of the polymers represent either an insulating or a semiconducting state. Figure I-11 gives an overview of the conductivities of a variety of conducting materials.

![Conductivity chart of various polymers, compounds and elements](image-url)
Theoretical background

The polymers can be converted to the electronically conductive (doped) state via oxidation or reduction reactions.

Electrical conduction in organic polymers occurs through the movement of either electrons or ions. In each case, the conductivity \( \sigma \) is the product of the carrier mobility \( \mu \), its charge \( q \) and the concentration \( n \) (of the carriers):

\[
\sigma = \mu \cdot q \cdot n
\]

[1-54]

Various models were developed to explain the electrical conductivity such as ionic conduction, band-type conduction, hopping conduction and others\(^5\). The exact mechanism of conductivity is not completely understood yet. Different approaches to describing important aspects of the conductivity mechanisms can be distinguished:

One model explains the mechanism of conductivity based on the knowledge of conductivity mechanisms in charge-transfer complexes and low molecular radical ions\(^6\). The transformation occurs with p-dopants (oxidants) such as AsF\(_5\), TiCl\(_4\), I\(_2\), or BF\(_4\) that serve as electron acceptors or n-dopants (electron donators) like Na or K. Charge balance is accomplished by the incorporation of an oppositely charged counterion into the polymer matrix.

The conductivity in many conducting polymers was found to be associated with spinless charge carriers\(^6\). The sudden increase of conductivity with doping is associated with structural changes (lattice distortions) within the polymer and the formation of localised electronic states, so called solitons, polarons or bipolarons\(^6\). Removal (or addition) of one electron from or to the polymer results in the formation of radical cations (anions) and in combination with localised lattice distortions a localised electronic state (polarons) comes into existence. When a second electron is removed from (or added to) such a site the result is a dication (or dianion), or in general terms, the formation of a bipolaron.

In the case of polyacetylene, distortions of the electronic configuration lead to an unbound p-electron in a so called soliton state. Whereas the presence of one or two electrons in the soliton state leads to positive or negative charge carriers, the absence of electrons results in a neutral (non-conducting) state. Those delocalized charge carriers in combination with the delocalized \( \pi \)-electron system enable conductivity without the motion of concurrent charged ions.

Other investigators\(^6\) prefer a theory that describes the conductivity mechanism related to the electron transport in dispersed metallic materials. These dispersions behave somewhat similar to dispersions of conducting polymers. At a certain critical concentration of small primary particles with diameters of less than 20 nanometers so-called "dissipative structures" emerge and charge transfer occurs along network structures along a chain of self-assembling particles.
2.4.2 Polyaniline chemistry

The synthesis of polyaniline can be carried out by chemical or electrochemical oxidation and dehydrogenation of aniline.\textsuperscript{65,66,67} This way a quinone diimine is formed. The oxidation of the primary aromatic amine leads to more complex quinone imines to give the final product, polyaniline. MacDiarmid et al.\textsuperscript{68} suggest that the polymer can exist in a wide range of structures, which can be regarded as copolymers of reduced (amine) and oxidised (imine) units.

![Image of Emeraldine salt](image)

Figure I-12: Emeraldine salt

Most commonly polyaniline is prepared by oxidative polymerisation of aniline using ammonium peroxydisulfate (NH₄)₂S₂O₈ as oxidant, dissolved in an aqueous acid medium (HCl, H₂SO₄, C₇H₈O₃S). The polymerisation process creates a conjugated polymer that consists of alternately repeating reduced and oxidised aniline monomers.

The "as synthesised" polyaniline exists in the completely doped exchange state. The protonated salt form is presented in Figure I-12, where A⁻ is representative of anions like Cl⁻ or SO₄⁻². The imine nitrogen atoms can be protonated in whole or partially to give the corresponding salts.\textsuperscript{69} The polymer is fully protonated if 50% of the imine nitrogens are protonated. Complete protonation of the imine nitrogen atoms in emeraldine base results in the formation of a so-called polysemiquinone radical cation. Simultaneously with doping the conductivity increases by the factor $10^{10}$.

In the doped state polyaniline is completely insoluble in any solvent. Treatment of the emeraldine salt with NH₄OH leads to the deprotonated non conducting base form of the polymer (cf. Figure I-13).

![Image of Emeraldine base](image)

Figure I-13: Emeraldine base

In the non-doped state the emeraldine base is well dispersible in various organic solvents like DMSO, NMP or m-cresol. By dedoping the polymers the conductivity is reduced to $10^{-10}$ S/cm into the range of insulating materials.
Theoretical background

The degree of protonation of emeraldine base can be controlled exactly by the choice of aqueous acid and its pH. With an oxidation state of exactly 0.5, polyaniline base and polyaniline salt are half-oxidised polymers. The average oxidation state of polyaniline, \((1-y)\), can be varied continuously from zero which represents the completely reduced leucoemeraldine (cf. Figure I-14),

\[
\text{Figure I-14: Leucoemeraldine}
\]

and up to 1S/cm to give the completely oxidised polymer pernigraniline (cf. Figure I-15).

\[
\text{Figure I-15: Pernigraniline}
\]

The conductivity and the temperature dependence of conductivity is considered to be in accordance with semi conducting mechanisms, but the mechanism of conductivity is electronic in nature\textsuperscript{70}.

Travers et al.\textsuperscript{71} suggests that conduction in polyaniline can be accounted for in terms of electrons hopping under the assistance of proton transfer, for which the presence of water is essential. Wessling et al.\textsuperscript{72} favours the description of a conductivity mechanism consisting of the sum of two effects: a metallic part and tunnelling from one particle to the next through a small 2nm-barrier.

The specific conductivity of polyaniline is in the range of \(10^{-10} \text{ S/cm}\) up to 10 S/cm. Polyaniline is a redox-active polymer: green-coloured in the conducting state, it can change the colour simultaneously with the conductivity under the influence of various media. Under basic and reducing conditions thin layers of non doped polyaniline are blue, doped layers are green, and the reduced form is transparent or slightly yellow.
2.4.3 Other basic applications and properties of polyaniline

Just as the other conducting polymers, polyaniline is insoluble in any solvent, it does not melt, and for this reason is unmouldable\textsuperscript{73,74}.

Therefore, polyaniline can not be processed like common thermoplastics: polyaniline can be processed by dispersing it in suitable dispersion agents\textsuperscript{65}.

Wessling \textit{et al.}\textsuperscript{75,76} suggest to overcome these problems by the means of dispersion technologies. This includes controlled polymerisation to provide a reproducible source of the polymer, controlled processing after polymerisation (i.e. drying, ion exchange, grinding, dispersion) and the choice of suitable agents, preferably those that are easy to handle, commonly available with reasonable costs, and with environmentally harmless properties.

For this reason, the starting point for most of the application areas (e.g. corrosion protection, coating of circuit-boards or LED-devices)\textsuperscript{77} is polyaniline, dispersed in various (organic) solvents (see also I-2.5.3).

If the intrinsic properties (i.e. EMI-shielding, antistatic properties) shall be transferred to other polymers, polyaniline can be dispersed in these materials.

Regarding its electrochemical behaviour, polyaniline is a highly reactive polymer. Classified as metal in the electromotive series, it is more noble than iron or copper and can be grouped close to silver.

The specific properties of polyaniline are based on the polyanionic structure, and the specific morphology, that can be modified by controlled doping or dedoping by introduction or removal of anions with different sizes or shapes.

Thus also the production of components with other polymers allows the exact creation of cavities in the corresponding polymer-compounds. The properties and areas of application of functional layers based on conducting polymers follow as a consequence of the ionic structure, morphology and the electron- and ion-conductivity or a combination of these properties. In contrast to other electrically conducting polymers, polyanilines may also be doped with protons\textsuperscript{78}. That raises interest in this material in the area of hydrogen technology, especially the application in fuel cell systems\textsuperscript{79,80}.

Other potentials and already realised applications for polyaniline are e.g. batteries\textsuperscript{81,82}, electrochromic devices\textsuperscript{83} (smart windows), and gas sensors\textsuperscript{84}.
Theoretical background

2.4.4 Support materials

Porous membranes contain fixed pores and the selectivity is mainly determined by the dimensions of the pores. The requirements for the polymeric support materials are not only determined by the flux and selectivity, but also by chemical, thermal and mechanical properties.

For solution-diffusion membranes, permeability is defined as the product of the solubility and diffusivity. High-selectivity membranes for gas separation often show low permeability whereas high permeability occurs at the expense of selectivity.\(^{85}\)

One way to get membranes yielding high flux and high selectivity can be approached by the combination of a microporous support structure with a selective top layer. Thus the advantages of individual materials can be combined: a mechanically robust and porous basic structure combined with the mostly much less permeable, but highly selective top layer.

The choice of materials can affect adsorption, chemical stability and the adhesion to the combined materials. Typical materials frequently used for membrane formation are polyimides, poly(vinylidenfluorides), celluloseacetates, polyacrylonitriles and others.

Various kinds of production processes for gas selective membranes (as described in Chapter I-2.5.3) allow the creation of membranes meeting the basic requirements of a thin and defect-free top layer and a sub layer with a negligible resistance. Table I-3 illustrates some typical support materials and their thermal properties.

The combination of the two layers can be realised technically e.g. by common production techniques:

- solution casting
- dip-, spray-, or spin coating
- plasma polymerisation
- interfacial polymerisation
- immersion precipitation

_Solution casting_ and _dip-, spray-, or spin coating_ are techniques that apply a polymer on another thin polymer layer. During the drying process the solvent evaporates slowly. The evaporating solvent vapour finally creates the porous structure. Parameters such as solvent type, temperature and evaporation time affect the resulting support structure.

During the _plasma polymerisation_ process an ionisation reactor forms various kinds of radicals that are capable of reacting with each other. The result is a precipitate on a support that finally represents the thin and permselective layer.
Theoretical background

The combination of materials by *interfacial polymerisation* creates a polymer compound consisting of a chosen support material with a selective top-layer that is polymerised onto the support. In this case the polymerisation reaction occurs between two reactive monomers at the interface of two immiscible solvents that are deposited on the support. This way a dense and thin layer can be formed on one side of the support material.

*Immersion precipitation techniques* use the different miscibility of polymers in various solvents or mixtures of solvents. Desired morphologies can be obtained by immersion of a polymer/solvent mixture in a nonsolvent coagulation bath and the choice of immersion time, temperature, etc.

Table I-3: Thermal properties ($T_g/\degree C$ and $T_m/\degree C$) and chemical structures of selected support materials

<table>
<thead>
<tr>
<th>Material</th>
<th>R</th>
<th>$T_m/\degree C$</th>
<th>$T_g/\degree C$</th>
<th>Chemical Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylcellulose</td>
<td>$\text{C}_2\text{H}_5$, Ethyl</td>
<td>150-160</td>
<td>43</td>
<td><img src="image" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Celluloseacetate</td>
<td>$\text{H}_3\text{C}_2\text{O}_2$, Acetate</td>
<td>240-290</td>
<td>80</td>
<td><img src="image" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Polyetherimide</td>
<td>-</td>
<td>-</td>
<td>210</td>
<td><img src="image" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Polyacrylonitrile</td>
<td>-</td>
<td>317</td>
<td>120</td>
<td><img src="image" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Poly(vinylidenfluoride)</td>
<td>-</td>
<td>178</td>
<td>-40</td>
<td><img src="image" alt="Chemical Structure" /></td>
</tr>
</tbody>
</table>
2.4.5 Coating with polyorganosiloxanes

Polyorganosiloxane is a general expression for a large group of synthetic polymeric materials in which silicon atoms are linked via oxygen atoms, each silicon atom bearing one or several organic groups (i.e. methyl, ethyl or phenyl groups) to form chains or network-like structures. The simplest representative of the group of polyorganosiloxanes is polymethylsiloxane (cf. Figure I-16). Polyorganosiloxanes are well-known materials in gas separation applications. Membranes for gas separation have high requirements concerning microporous defects. The presence of only a small number of pinholes often results in a dramatic loss of selectivity.

During the production of polyaniline membranes, the creation of defects or damages in the perm-selective polyaniline layer cannot be completely avoided, especially if the membrane areas become larger (> 20cm²).

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{Si} & \quad \text{O} & \quad \text{Si} & \quad \text{O} & \quad \text{Si} & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 & \quad n & \quad \text{CH}_3
\end{align*}
\]

Figure I-16: Polymethylsiloxane

To avoid microporosity, the membrane surface can be "sealed" with commercially available polyorganosiloxanes.

The overall selectivity should not be affected by this treatment: even if the selectivity of the silicone within the plugged pores is low, the pore area is microscopic compared to the over all area of the membrane.

2.4.6 Tensile properties of thin films

In general, the degree of order in plastics is very similar to that of low-molecular mass compounds. There are amorphous, crystalline, and semicrystalline phases, which exhibit short- and long-range order in one, two, or three dimensions.

A peculiarity of polymers is that amorphous regions are also present in the crystalline state and the crystallinity can be varied over a wide range. Mechanical properties, such as the elasticity and the toughness of polymers are mostly determined by the connectivity and entanglement of the molecules. Polymers in the glassy state and in the isotropic melt generally have a low degree of order, they are amorphous.
Theoretical background

Important information on the mechanical state of polymers can be obtained with standardised mechanical tests such as those proposed by ISO or DIN.

Tensile forces that are applied to test specimens result in various structural changes occurring within the test sample. On a molecular scale, at the beginning the main bonds are "stretched" elastically. With rising tensile stress an entropy-elastic deformation of the polymer can be observed. Further increase of the forces loosens the molecular network (macromolecular loops) and finally results in an irreversible loss of intermolecular connections.

These processes are visible in a tensile / elongation diagram that is obtained by standardised test procedures. During a test, a constant force is applied to the sample and the elongation of the test specimen is measured. Important coefficients to express mechanical properties are

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma$</td>
<td>tensile stress</td>
<td>(N/mm²)</td>
</tr>
<tr>
<td>$\sigma_t$</td>
<td>tensile stress at break</td>
<td>(N/mm²)</td>
</tr>
<tr>
<td>$\sigma_x$</td>
<td>tensile stress at % strain</td>
<td>(N/mm²)</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>tensile strain</td>
<td>(%)</td>
</tr>
<tr>
<td>$\varepsilon_t$</td>
<td>tensile strain at break</td>
<td>(%)</td>
</tr>
<tr>
<td>$E$</td>
<td>e-modulus</td>
<td>(N/mm²)</td>
</tr>
</tbody>
</table>

where the e-modulus $E$ is calculated on the basis of two defined tensile forces and the respective elongation values:

$$E = \frac{(\sigma_2 - \sigma_1)}{\epsilon_2 - \epsilon_1}$$  \[I-55\]

The difference between thin films and thick samples under mechanical stress are discussed by Klemann and Bastida et al. According to the model of Anderson, a critical parameter $K_{IC}$ independent of the geometry of the sample has been defined,

$$\ell_1 = 2.5 \cdot \left( \frac{K_{IC}}{\sigma_y} \right)^2$$  \[I-56\]

where $\ell_1$ is the film thickness at the transition range and $\sigma_y$ is the yield stress, the first tensile value in which an increase of elongation occurs without an increase of tensile stress.

The function $K_{IC}$ versus film thickness describes the transition of the stress modes in tensile tests from "plain strain" to a "plain stress" mode. For thin films $K_{IC}$ is constant. In a transition
Theoretical background

area, \( \ell < \ell_0 < \ell_t \), \( K_{IC} \) gets smaller with reduced film thickness, and the point \( \ell_t \) indicates the beginning of the area where \( K_{IC} \) again becomes constant with rising film thickness.

In thick test samples a three-dimensional deformation in the rupture area is suppressed by the surrounding material: a three dimensional tension and a strain in plane direction.

If the sample thickness \( \ell \) and the deformation zone in the rupture area have the same extension, the tension in plane direction and at the same time deformations in direction of the thickness allow the formation of a three-dimensional tensile state. Bastida et al.\(^{91}\) found by testing thin polyetherimide and polycarbonate films (0.1-2mm) and a rising film thickness, a decreasing e-modulus for \( \ell < \ell_t \) whereas the e-modulus for \( \ell > \ell_t \) was constant.
2.5 Separation Processes

The expression "membrane" (lat.: thin skin) has been used for more than 150 years for separation materials in diffusion experiments.

A membrane can be considered as a permselective medium that can induce selective transport between two phases. Provided a driving force is present (e.g. a concentration gradient), a selective separation effect is achieved because the membrane has the property to favour the transport of one component from the feed mixture over that of other components.

Figure 1-17 shows such a membrane process schematically. Usually a membrane separates two phases: phase A is considered as the feed or upstream side, while phase B is considered as the permeate or downstream side.

Membranes work as permselective barriers. They are employed in a variety of applications. The main membrane processes can be classified according to their utilisation and the application range.

Figure 1-18 and Table 1-4 give an overview of the relative size of the excluded media (atoms, molecules, macromolecules, ...) and the application range of various separation processes.

The processes of micro-, ultra- and nanofiltration are related to filtration techniques in which a solution containing dissolved or suspended solutes is filtered through a membrane. The solvent
passes through the membrane, the solutes are retained. These methods principally classify mixtures according to size of the particles.

The smallest pore size is used in reverse osmosis membranes. They are used to separate dissolved microsolutes, such as salt from water\textsuperscript{46}.

![Separation by:](image)

**Figure I-18:** Separation processes and their applicable separation ranges

Electro-Dialysis is a membrane process, in which charged membranes are used to separate ions from aqueous solutions under the driving force of an electrical potential difference\textsuperscript{46}.

Gas separation and pervaporation are separation processes performed by polymeric membranes. In the gas separation process, a mixed gas feed is passed across the surface of a membrane that is selectively permeable to one component of the feed. The membrane separation process produces a permeate that is enriched in the more permeable species and a residue enriched in the less permeable component. Membrane-based gas separations often require compression of feed streams to provide the driving force for permeation. The feed mixture consisting of two gases can be separated with a permeate being enriched with gas A and a residue with an increased amount of gas B. In technical use membrane systems often require recycling of some of the permeate or non-permeate streams.
Table I-4: Membrane processes and their separation ranges

<table>
<thead>
<tr>
<th>Process name</th>
<th>Separation range / μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas separation</td>
<td>&lt; 0.0004</td>
</tr>
<tr>
<td>Pervaporation</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>Reverse osmosis</td>
<td>0.001-0.002</td>
</tr>
<tr>
<td>Diffusion-Dialysis</td>
<td>0.001-0.002</td>
</tr>
<tr>
<td>Electro-Dialysis</td>
<td>0.0005-0.003</td>
</tr>
<tr>
<td>Nanofiltration</td>
<td>0.0008-0.008</td>
</tr>
<tr>
<td>Dialysis</td>
<td>0.0008-0.01</td>
</tr>
<tr>
<td>Ultrafiltration</td>
<td>0.002-0.3</td>
</tr>
<tr>
<td>Microfiltration</td>
<td>0.09-2</td>
</tr>
</tbody>
</table>

Pervaporation is a process in which a liquid mixture is put in contact with the membrane surface and the permeate is removed as vapour. This is obtained by keeping the vapour pressure of the permeate side of the membrane lower than the partial pressure of the feed liquid: A vacuum or a temperature difference are applied to create the driving force. The permeating component can then be removed by using a sweeping gas.

2.5.1 Membrane-based gas separation

The separation of compounds in the gas phase offers advantages over separation in a liquid phase. In liquid phase separation systems in which transport rates through the membrane are in the same range of those of the compounds within the liquid phase (i.e. ultrafiltration, reverse osmosis) an additional mass transfer resistance can build up on the membrane surface. High diffusion rates of gases in the gas phase generally do not allow the formation of a bulk layer on the membrane at the feed side (see I-2.2.3).

Furthermore, interactions with inert gases (except carbon dioxide) and the polymers can be neglected. Simple production techniques and a large variety of available polymer materials allow the production of process-tailored separation systems.
Theoretical background

2.5.2 Current state of membrane-based gas separation applications

Examples of gas separation technologies used in industry are given in the following and will highlight the importance of these systems for future membrane-based separation processes:

- One of the first membrane-based gas separation systems was used for hydrogen separation from ammonia purge gas streams\(^4\), and to adjust the hydrogen / carbon monoxide ratio in synthesis gas\(^5\). These applications have been successful since carbon monoxide, methane and nitrogen are highly supercritical and hydrogen has extremely high diffusion rates compared to these gases, e.g. the hydrogen / methane selectivity of selected polyimide and polyaramid membranes is about 200.

- Other interesting fields for hydrogen separation are petrochemical and refinery applications. In those systems the recovery rate of hydrogen and the amount of lost N\(_2\) and hydrocarbon is an important issue\(^6\).

- Membranes can be used to separate air to yield either oxygen or nitrogen enriched air. The nitrogen enriched air is obtained by controlling the fraction of feed air passing through the membrane and thus allowing sufficient oxygen to pass through the membrane to reduce its mole fraction to all desired levels\(^7\). Current membranes have an oxygen / nitrogen selectivity of 4 to 8.

- Gas separation membranes are being used for acid gas separations. The principal application in this category comprises carbon dioxide removal from a variety of gas streams containing primarily methane as the second component. A permeate consisting of 95% carbon dioxide and a retentate of 98.5% methane can be reached by this application\(^8\). It has been shown that multistage membrane systems can be competitive with recovery of carbon dioxide by conventional diethylamine (DEA) processes, even at carbon dioxide concentrations as low as 5%\(^9\).

- Other common compounds to be removed from natural gas are hydrogen sulphide (sour gas treatment) and water, that cause corrosion problems in pipelines. Also the separation of carbon dioxide increases the economic benefit by reducing the transport costs.

- Gas separation is used pursued in olefin / paraffin separation in hydrocarbon processing\(^10\), and the elimination of SO\(_2\) from smelter gas streams\(^11\).

- With a content of 0.005–8% natural gas offers a good source for helium production\(^12\). To avoid extremely low liquefaction temperatures for helium extraction, membrane technology is used for helium recovery from natural gas\(^13,14\).
Theoretical background

- Helium is also being recovered for reuse from diver's habitat gases. Commercially established systems are already on the market\textsuperscript{105}. Such systems are suited uniquely to eliminating nitrogen and oxygen with helium recovery rates of up to 95%.

- At present, hydrogen technology offers a developing field for potential gas separation systems. Portable small-sized hydrogen generators can be used for the final purification of hydrogen\textsuperscript{106}. Produced by electrolysis the gas pair H\textsubscript{2}/O\textsubscript{2} has to be separated efficiently\textsuperscript{107}.

- Proper functionality of PEM-membranes in fuel cells requires removal of CO from the reformer gas stream. Highly effective silver-palladium membranes can fulfil highest demands on purity\textsuperscript{108}.

- In biotechnology, the use of sterile oxygen-enriched air is often required as many fermentation processes directly depend on sufficient oxygen supply\textsuperscript{109}.

- The separation of water vapour from natural gas and other steams as well as the separation of organic vapours from non-condensable gases such as air and methane are both areas of current and future opportunities for membranes\textsuperscript{110}.

- Also gasoline vapour recovery from off-gas streams (e.g. in gasoline tanks or chemical processes) is a well established technology\textsuperscript{111,112}. In combination with absorption and PSA technologies, recovery rates of up to 99.99\% can be realised.

2.5.3 Membrane production techniques

Thin polymer films can be produced with a number of different methods. A broad overview over frequently used methods is given by Mulder\textsuperscript{46} and Okui\textsuperscript{113}.

Concerning the restricted processability of polyaniline with respect to membrane processing, the particular properties of intrinsic-conducting polymers must be considered:

Solvents that are proposed as suitable dispersants for polyaniline\textsuperscript{82,114} are aqueous acetic acid, or m-cresol, tetrahydrofurane (THF), dimethyl formamide or N-methylpyrrolidone (NMP).

According to publications polyaniline membranes have only been produced from polyaniline-NMP dispersions. Li et al.\textsuperscript{115} reported about the formation of films from different polyanilines dispersed in various solvents, but none of them was self-supporting.

With commercial availability of a reproducible source, in this work PAni-NMP dispersions of ORMECON will be used. The film formation process is influenced by interactions between the polyaniline, the solvent and the substrate on the one hand, and the influence of temperature, evaporating rate and others on the other hand.

This raises questions of how to choose the processing parameters that determine the membrane qualities:
Theoretical background

- does a dense polyaniline layer come into existence?
- does the dispersion spread on the substrate?
- will support materials be affected by NMP?
- will fused materials be stable during drying or doping processes?
- do acid groups on the surface of the substrate dope polyaniline?
- what happens during solvent evaporation?
- will the temper process affect support and film materials?

For this work the solution casting method was chosen to create thin membranes. This method is well established and process parameters can be controlled easily. In the following this method and also alternative production techniques will be presented, as well as theoretical aspects of film formation.

2.5.3.1 Phase inversion

In general, phase inversion is an expression for a production method that transforms a polymer from a liquid to a solid state. A controlled phase transition process (i.e. the rate of phase transition) allows to determine the morphology of the membranes.

To produce membranes with this method, homogeneous solutions of the polymers in (single) solvents or mixtures of solvents and non-solvents are prepared. Phase inversion is achieved by solvent evaporation, exposure to an excess of nonsolvent, and thermal gelation. Symmetric and asymmetric as well as porous and non-porous membranes can be formed this way.

The phase inversion technique includes various modifications that are explicitly explained by Baker.116

With respect to producing polyaniline-films this method is not applicable: precipitation of polyaniline particles will occur a few moments after mixing the dispersion with other solvents in a way that film formation is impossible.

2.5.3.2 Solution casting

This method is a special kind of phase inversion and the most simple one.

In this preparation technique a polymer-solvent mixture is spread on an even and smooth support, e.g. glass plates, metal drums, or porous carriers such as tissues or ceramics. Controlled evaporation of the solvent into a non-reactive atmosphere allows formation of homogeneous
and dense membranes. The solution is often covered so that the vapour is removed slowly to prevent bubbles, and with this cavities in the forming film. A comparable membrane formation process can be achieved by deposition of polymers on substrates with dip-coating or spray-coating techniques. Rests of solvents in the film can often be removed by a temper process. Various process parameters such as the choice of solvent(s), polymer concentration temperature, evaporation time, and others determine the structure, properties and morphology of the films. Interactions between the liquids and the substrate surfaces have to be considered. Also an understanding of the film formation process in molecular dimensions is necessary.

2.5.3.3 Spin coating

In this technique the support to be coated is fixed on a rotating disk. The polymer solution is applied to the carrier and spread uniformly by rotational forces. Film formation is finished when the solvent has been evaporated. The choice of rotation speed, solvent concentration, evaporation time and molar mass allows to create films with various thicknesses. According to Pethrik\textsuperscript{17} the film quality depends on the product viscosity $\eta$ and the polymer concentration, $c$. An optimum is given for

$$c \cdot \eta = 1$$

Spin coating allows to produce films in a range from about 2nm up to more than 30µm. Concerning polyaniline processing this method might be applicable. The question arises why to prefer this method to solution casting as long as no clear advantages for production of lab scale can be seen.

2.5.3.4 Water casting

This method uses the interdependence of energies of interfacial areas of different solvent phases and gravity: a certain amount of solution is applied to the surface of water and either a film or drops or bubbles form. When the solvent is being evaporated the polymer forms a film on the water surface. Dependent on the desired application area the film can be transferred on suitable support materials\textsuperscript{118,119}. Small amounts of water will result in instantaneous precipitation of polyaniline particles. With a density of about 1.4g/cm$^3$ the precipitate just accumulates at the bottom of the water bath without forming a film.
2.5.3.5 Langmuir-Blodgett films

The Langmuir-Blodgett (LB) technique is a technique commonly used to produce highly ordered, ultrathin-layered films of low molecular substances, but also with amphiphilic polymeric materials. Substances for the LB technique often consist of a long alkyl chain with a hydrophilic head group.

By first depositing the amphiphilic material, dissolved in a volatile solvent immiscible with water, films are prepared on the surface of water (or other solvents). When the solvent has evaporated, the organic molecules may be compressed by a floating barrier to form a film. Because of the molecular forces the individual molecules align themselves during this process and raise up in a way that needs a minimum of area.

For coating, a substrate is placed carefully under this layer and the molecule layer is transferred to the substrate surface. It is possible to provide specific states of packing of the molecules on the substrate by choosing suitable transfer conditions (e.g. temperature, vapour pressure,...). Besides the creation of highly uniform and defect free monolayers also bi- and multilayers can be created by repetition of the coating process as described.

A monolayer can be described as a layer of molecules that consists of a molecular layer with molecules that are orientated in the same direction as the hydrophobic part of the support material (head-to-tail orientation). The expression "bilayer" is used in the case of a head-to-head or tail-to-tail orientation of the molecules: the repetition unit then is one of those conformations\textsuperscript{120,121}.

LB-techniques applied to the production of polyaniline membranes on surfaces of liquids have not been reported, yet. It is likely that solvent-polyaniline interaction obstructs any film formation (as discussed in I-2.5.3.4).

2.5.3.6 Theory of film formation

All film formation processes start with the material being dissolved. Solution casting is a technique in which a dissolved polymer solution is spread on a suitable carrier. The evaporation of the solvent forces the polymer to agglomerate, and finally to form a film.

The fundamental relation between the surface energy $\gamma$ of two condensed phases (here: solid and liquid) is expressed by the Young-Duprée quation\textsuperscript{122}

$$\gamma_s = \gamma_{sl} + \gamma_L \cdot \cos \theta$$
Theoretical background

where $\gamma_{SL}$ is the interfacial energy between solid and liquid phase, $\gamma_S$ and $\gamma_L$ the surface energies of the solid and liquid phase, and $\theta$ the contact angle between the phases.

The contact angle can be seen as a quantitative measure of wettability. Complete wetting of the solid phase occurs if $\theta = 0$; in this case the expression that describes the energy balance is:

$$\gamma_S - (\gamma_{SL})_c + \gamma_c = 0 \quad [I-59]$$

where $\gamma_c$ is the critical surface tension and $(\gamma_{SL})_c$ the critical interfacial tension$^{123}$. If the energy balance becomes positive the solution spreads on the surface whereas a negative balance results in the formation of a drop upon the substrate and spreading (or film formation) does not occur.

Zhang et al.$^{124}$ propose a model for film formation which starts with a polymer solution. Evaporation of the solvent forms an anisotropic gel phase and finally a solid membrane comes into existence.

This process is explicitly outlined is by H. Käufer$^{125}$: the initial point of film formation is a dilute polymer solution. The process itself starts with successively evaporating the solvent. During this process the polymer concentration is rising slowly and in a transition state a gel phase can be observed. At this point (below the glass transition temperature) the actual state of the molecular structure is fixed and a solid polymer film is forming (cf. Figure I-19).

The anisotropy comes into existence by a difference between molecular differences in the molecular dimensions vertical and parallel to the surface level of the film.

The orientation of the macromolecules to the film level in thin polymer films has been discussed in various articles$^{126,127}$. The investigators found out that the chain-axes preferably arrange themselves in the same level as the film-axis.

Russel and Gugger$^{128}$ name the resulting structure "in-plane orientation" or "uniplanar structure". The proposed model describes the anisotropy of solution-casted films. The molecular dimensions are comparable to film made by means of other techniques.

Research of Song et al.$^{129}$ showed that films produced by solution casting had a precisely parallel-orientated layer structure. During film formation from the solution, self-assembling of the molecules was observed. The molecule chains tend to form parallel structures. According to Song et al., strong $\pi-\pi$ interactions between neighbouring (not covalently bonded) rings are responsible for this behaviour. In this case the ring level of the polymer repetition unit is orientated vertical to the film, whereas the axis of the polymer and the film level have the same ori-
Theoretical background

entation. This phenomenon was not observed in films made by extrusion. It was assumed that the influence of processing superimposes the influence of film thickness.

Figure I-19: Schematic representation of film formation from solution: the assembly of macromolecules during film formation, proportion of the molecular dimensions

Despotopolou et al.\textsuperscript{130} found a correlation of film thickness and structure. On spin-coated poly-di-(n-hexylsilane) films, the position of the polymer backbone and structural changes with varying film thicknesses were investigated.

IR examinations led to the conclusion that the polymer chains arrange themselves in a conformation parallel to the film surface. With decreasing film thicknesses an increase of disorganisation of the side groups was found and from $\ell < 50\text{nm}$ irregularities in the conformation of the polymer chains were observed. At the same time the ratio of the crystalline phase was decreasing with decreasing thickness. The conclusion was that the starting stage of crystallisation is influenced by the substrate surface or the restricted geometric conditions.
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3 Experimental methods

3.1 Sample characterisation

3.1.1 Determination of sample thickness
An exact determination of the membrane thickness is necessary for calculating permeability. The thickness can either be measured by means of a micrometer screw, or alternatively by microscopy. The micrometer screw can be used if an accuracy of +/- 1µm is sufficient. In the case of films thinner than 10µm, the use of microscopy turned out to be a suitable method with an accuracy of about 0.2µm.
The thickness was generally measured after the permeation tests. To get high accuracy results the membrane was cut into four small strips. The thickness was determined as an average thickness at four defined positions on the membrane, as illustrated in Figure II-1. The sample was prepared with adhesive-tape on both sides. The piece of film was fixed between the two strips of tape that were to be slightly longer than the specimen. This sample was then cut into two pieces. Thus it was possible to see the end of the tape exactly. This was important since now the sample could be placed exactly vertical on the microscope slide by means of a little clamp and there was a clear distinction between the edge of the membrane and the beginning of the tape. Now the thickness could easily be read from a graduation scale in the lens, and the average thickness could be calculated.

Figure II-1: Exact determination of the average membrane thickness at four positions

3.1.2 Measurement of specific conductivity
The electric conductivity of polyaniline directly correlates with the doping state of the polymer. Four-point methods such as the van der Pauw test method provide high reliability. This is always of special interest if the transition resistance (electrode to sample) is not known, or if polarisation during measurements may occur.
Experimental Methods

For each test three disc-shaped samples of polyaniline film with a diameter of 1.4cm were prepared and measured separately. To get highest reproducibility, five different voltages were applied to each sample to determine the average specific conductivity $\sigma_{AM}$.

Before each test the samples were dried at 100°C for one hour and then were exposed to atmospheric conditions for one day.

### 3.1.3 Sample preparation for UV-Vis and ATR-IR

Doping of polyaniline changes its visible appearance and the IR absorbance. The use of spectroscopic methods allows identification of various doping states of polyaniline since the transmission in the UV-Vis-IR range ($\lambda = 300-3000\text{nm}$) is directly related to the doping state (doped or undoped) and the degree of doping. UV-Vis examinations were carried out with a Perkin Elmer Lambda 15 spectrometer.

Ideally, a thin and optically transparent polyaniline film is placed on the sample holder and then is gently dried in a drying cupboard at 30°C for one hour.

Doping was accomplished by exposing the membrane to gaseous HCl for two minutes, followed again by a gentle drying process.

IR examination was performed by using a Bruker Equinox 55 ATR-IR measuring system.

For IR analysis the samples were dried carefully overnight at 30°C and, after this exposed to atmospheric conditions for a few hours. The computer-supported spectrometer was combined with an automatic peak detection system. The scan rate for each sample was 30 seconds.

### 3.1.4 Sample preparation for MALDI-TOF-MS

Complex organic molecules can be examined by the use of gentle desorption / ionisation methods. Matrix-supported laser desorption / ionisation (MALDI-MS) is such a method, in combination with time-of-flight (TOF) mass spectroscopy.

This type of examinations is usually used to get a deeper insight into the structure of sensitive and fragile organic biopolymers such as DNA.

In this case polyaniline base dispersed in NMP was examined. 0.1ml of polyaniline dispersion were mixed with 10ml of 2.5-dihydroxy benzoic acid (DHB, 50g/l distilled water). The mixture was placed onto a metallic sample holder. During evaporation of the solvent the polyaniline particles get fixed in the DHB matrix. Successive abrasion of the matrix and the embedded polyaniline release the sample and its fragments into the mass detector. The instrument used was a Bruker Daltonik MALDI-TOF-MS.
3.1.5 Preparation of samples for BET examinations

On account of the sorption modes the determination of the specific surface is quite important as well as the estimation of the size of polyaniline particles. Furthermore, information can be obtained as to whether differences exist between films and powders. Sorption data give a deeper insight into the sorption modes and the structure (i.e. porosity) of the polymer.

The measurement requires essentially dry samples. An empty sample holder was weighed before being filled with polyaniline samples. Approximately 0.2-0.4g of the sample (powder or film) were weigh and filled into the sample vial. After this the samples were placed in the apparatus and dried and evacuated (125°C, 10^{-5}Torr) overnight. The dried sample was weighed again and then put into the BET measuring system. After cooling down to the temperature of liquid nitrogen (77K) and evacuation overnight, the BET tests were started.

The apparatus for BET examinations was an ASAP 2010 V3.00 D measuring system. The tests were performed overnight using standardised test procedures. The measured data were stored automatically by a personal computer. The specific surface was then calculated from this data on the basis of BET and Langmuir sorption models.

3.1.6 SEM and EDX characterisation

In scanning-electron microscopy (SEM)\textsuperscript{1,2} a small electron probe scans in a raster across the surface of the specimen. The incident electrons are scattered by the test object. Electrons leave the specimen as backscattered electrons, but some electrons can leave the specimen as secondary electrons from the surface layer.

The ionisation of inner atomic shells results in the emission either of characteristic X-ray quanta which can be related to the corresponding atoms (EDX analysis), or of Auger electrons.

The image is generated by the signal of emitted secondary electrons, backscattered electrons, Auger electrons, absorbed specimen current, or X-ray quanta.

Electron micrographs of membranes were taken and x-ray microanalysis (EDX) performed using a low-magnification scanning-electron microscope (SEM), Cambridge Stereoscan 360, accelerating voltage 20kV.
3.1.7 Content of water

If polyaniline powder and membranes are stored under room conditions the question arises as to the extent of sorption of molecules from the ambient atmosphere.

For BET tests, completely water-free samples were required. The difference between weight before and after the drying process allows the estimation of percentage of water in the polymer. The tested samples were stored at room atmosphere for 2 weeks. The samples were weighed before and after degassing for 12 hours at 125°C and 10⁻⁵ Torr, and the difference in weight was related to the amount of adsorbed water.

3.1.8 Specific gravity

For evaluation of gas sorption data with respect to the gas solubility in the polymer and for calculation of the solubility coefficient, it is necessary to know the specific gravity of the material. This value was measured with a Micromeritics helium pycnometer.

Before the tests were performed, the samples were stored under ambient room conditions for 2 weeks. 0.3-0.6g of the sample was weighed out in the case of polyaniline films, and in the case of polyaniline powder, 0.5-0.7g of sample were used.

3.1.9 Measurement of permeability

3.1.9.1 Standard permeation test

Permeability data were determined with the constant volume method under steady-state conditions. The system design was in accordance with manometric permeation testing systems as described in e.g. 34. A schematic illustration is shown in Figure II-2.

If gas is filled into the upstream part of the diffusion cell, the transport of the gas through the test membrane is indicated by a pressure increase as a function of time.

Before each test run, the permeation assembly was degassed overnight to 10⁻⁴ mbar using an oil rotary vacuum pump (vacubrand) in order to eliminate effects of adsorbed compounds in the membrane.

The tests were carried out under isothermal conditions at 21°C (± 1°C). Gases (H₂ / O₂ / CO₂ / N₂) were obtained from Linde and their purity usually exceeded 99.99 Vol.-%. For permeation studies, an upstream pressure of 1-7bar was used.

Vacuum valves make it possible to keep leaking of atmospheric gases into the test cell at a minimum. A diaphragm pressure gauge was used to determine the upstream pressure, and an-
other high-accuracy pressure indicator (*MKS Baratron*, range 0.001-10 mbar) to measure the permeant pressure in the downstream volume.

The test assembly was planned to allow for flexibility in testing: variable cell volumes, as well as permeation areas can be adjusted. Thus it was also possible to test various sample thicknesses and to apply pressures of up to 7 bar.

The diffusion cell consisted of two half-cells made of brass. The membrane sample to be tested was placed on a sintered metal disc between the two half-cells.

![Diagram](Figure II-2: Standard gas permeation test assembly)

Then the two parts were connected and sealed together with a vacuum-tight, flat O-ring and a rubber seal. The diameter in the middle of the O-ring and the rubber seal defined the cross-sectional area for permeation.

It also seemed sensible to test the seals and the test samples for leaks by pressurising the feed side up to five bar of nitrogen (and hydrogen) and observing the rate of increase of pressure on the permeate side. A sudden increase of pressure indicates leaks or microporous defects in the membranes, as well as a resulting separation factor $\alpha_{12/N_2}$ of approximately 4.

If no sudden increase was observed, the cell was again evacuated. Usually, the pressure decreases to $10^{-3}$ mbar after one hour, and reaches $10^{-4}$ mbar after 24 hours.

Before being tested, the polyaniline films were pressed between filter papers for several days to get them flat and were then dried carefully. After drying for a minimum of 24 hours and degassing the permeation cell, the sample was ready for testing.

The test procedure used included the following steps performed in succession:

- switching on multimeter and pressure indicator 15 minutes before each test run
- closing valves of upstream and downstream volume and recording pressure increase
Experimental Methods

- choosing desired upstream pressure
- opening valves on the upstream side to start the permeation experiments

In step 2 the data were collected for 30 minutes to get the inherent leak rate. This was done to get a reference for calculating the permeation rate and to get a set of leak rates to calculate the average leak rate.

The leak rate is also a measure for the sensitivity of the diffusion cell, since the lower limit of resolvable permeation is set by its value. The upper limit for permissible leak rates was 0.2Pa/hour.

Data acquisition was performed with a multimeter (Volcraft) and the data were collected by an IBM-type personal computer. For evaluation and analysis, the experimental data were calculated with standard office software (Microsoft EXCEL 7.0).

The estimated errors vary with a various number of factors, e.g. the magnitude of gas flux, the kind of membrane or the test gas, to name a few.

The potential error of the test cell in gas permeability tests for individual measurements are approximately 10% in the case of hydrogen and carbon dioxide, and up to 15-20% in the case of slowly permeating gases such as oxygen and nitrogen (see also Error Discussion).

3.1.9.2 Calibration of the measuring system

To assess the volume of the test chamber, the geometric parameters were measured.

The downstream volume then was determined with high accuracy by using a manometric method:

The downstream part was sealed with a rubber plate from the feed side. Then the cell was evacuated. Once steady state was reached, the valve of the vacuum pump was closed and the cell was connected via a vent to a gas chamber with known gas volume and pressure.

A second vent or capillary in the extra gas chamber was then opened and the pressure inside the two connected volumes rose. The same test was then done again, but only with the calibration volume. From the quotient of the slopes of the \( p \) vs. \( t \) curves for the volume to be determined and the two volumes connected together, the unknown cell volume could be calculated.

The pressure range for the tests was 0-2mbar and isothermal conditions were guaranteed by placing the test assembly into an insulated box.

A set of 5 calibration runs was performed to calculate the downstream volume \( V_x \), using the following equation:
where $V_c$ is the calibration volume, $\Theta_4$ is the slope of the initial pressure and $\Theta_b$, the slope of the pressure increase in the connected volumes ($V_c + V_s$).

The geometric cell constants determined were used the calculation formula, which made it possible to calculate the permeability at the end of each test run.

### 3.1.9.3 Differential pressure method

An alternative gas-permeation test method is based on differential pressure measurement.

The differential pressure cell consisted of two sections separated by the membrane. A porous metal disk was placed at the low pressure side of the cell to support the membrane. In order to seal the compartments of the cell from the ambient atmosphere, silicone or rubber O-rings were placed between the support and the membrane.

![Figure II-3: Permeation test assembly based on differential pressure measurement](image)

The pressure in the upstream volume was monitored by a pressure gauge (1-5 bar).

The downstream part of the membrane was exposed to atmospheric pressure and connected to a differential pressure sensor (Furness Controls LTD, FCO 40, range 0-2 mbar).

By maintaining a constant pressure difference between the two sides of the membrane, the pressure increase in the downstream part could be observed. In contrast to the time-lag and the constant volume / variable pressure method, the downstream part was not evacuated.

The permeation test started exactly at that moment, when the vent which connected the downstream part with the atmosphere was closed. Gas that permeated through the membrane was indicated by an increase of the downstream pressure against the atmospheric pressure.
A typical test run was within a pressure range of 0-4mbar of overpressure in the downstream compartment. After each run the gas that had entered the downstream part via the membrane was released into the atmosphere.

After a number of runs an equilibrium state was reached at the membrane, and the pressure increase in the downstream volume was recorded versus time.

When the cell constants and the slope of the $p$ vs. $t$ plot are known, it is possible to calculate the permeability of each gas.

For calculations it must be considered that the driving force for permeation in this test method depends on the difference of the partial pressures of the tested gases so that the gas composition in the downstream side must be known.

### 3.1.9.4 Calculation of permeability

The permeability coefficient was measured under steady state conditions and calculated from the slope of the $p$ - $t$ curve.

With knowledge of the chamber volume and the feed gas pressure applied, the accumulation of gas in the low-pressure part could be related to the permeability. The corresponding formula and parameters that were typically used are listed in the following:

$$ P = \frac{V_A \cdot T_0 \cdot \ell}{(p_1 - p_2) \cdot A_M \cdot p_0 \cdot T_A} \cdot \left( \frac{\Delta p}{\Delta t} \right)_s $$

with

- $\ell$: membrane thickness $10^{-3}$cm
- $p_1$: pressure on the upstream side $10^5$Pa
- $p_2$: pressure in the downstream volume $10^6$Pa
- $p_0$: standard pressure $1.013 \cdot 10^5$Pa
- $A_M$: membrane area $7$cm$^2$
- $T_0$: temperature under STP conditions $273.15$K
- $T_A$: downstream temperature $293$K
- $V_A$: downstream volume $147$cm$^3$
- $(\Delta p/\Delta t)_s$: slope at steady state of $p$ - $t$ graph $0.005$Pa/s

The permeability can be expressed in SI-units, $P = \left( \frac{\text{cm}^3 \text{STP} \cdot \text{cm} \text{polymer}}{\text{cm}^2 \text{polymer} \cdot \text{s} \cdot \text{Pa}} \right)$. 

73
Many publications prefer the use of the unit *Barrer*:

\[
1 \text{ Barrer} = 10^{-10} \frac{\text{cm}^3\text{STP} \cdot \text{cm polymer}}{\text{cm}^2\text{polymer} \cdot \text{s} \cdot \text{cmHg}} = 7.4 \cdot 10^{-4} P \text{ (SI-units)}
\]

If the permeability is small or/and the flux does not need to be related to the membrane thickness, the permeate flux may also be expressed as \( J = \left( \frac{\text{cm}^3\text{STP}}{\text{cm}^2\text{polymer} \cdot h \cdot \text{bar}} \right). \)

### 3.1.9.5 Determination of time lag

Before reaching steady-state conditions, the permeation process has to overcome a transient state. This time span is called "time lag", \( \tau. \)
This parameter can be determined by the interpolation of the \( p - t \) curve at steady-state conditions to the time axis (cf. Figure I-5). The intercept on the time axis is commonly known as the time lag.

### 3.1.9.6 Temperature dependence

In order to get temperature-related permeation data, the permeation cell was put into a thermostatted drying cabinet. The accuracy of the temperature was stated to be +/- 0.1°C.
Before permeation experiments started, upper and lower sides were evacuated to < 10⁻³mbar and simultaneously heated up to the desired temperature. The temperature range was 25-65°C and the gas was applied to the membrane with a pressure of 2.8 bar absolute. The pressure data were measured with an *Edwards BAROCCEL Type 600* pressure sensor, range 0.1-100Torr, and recorded by a personal computer.
The apparent activation energy for permeation was then calculated from the Arrhenius-type equation for permeability (see also Chapter I-2.2.1).

\[
\ln P = \ln P_0 - \frac{E_a}{R \cdot T}
\]

where

- \( R \) universal gas constant (J/mol K)
- \( T \) temperature (K)
- \( E_a \) activation energy (J/mol)
- \( P_0 \) permeability at STP \( \left( \frac{\text{cm}^3\text{STP}}{\text{cm}^2\text{polymer} \cdot h \cdot \text{bar}} \right) \)
In order to determine the activation energy, the permeation data is expressed in an $\ln p$ vs. $1/T$ plot. Now the activation energy can be calculated from the slope of this curve.

3.1.9.7 Validation tests with the constant volume / variable pressure method

This method (in the following chapters named "CVVP" method) was used for comparison to some of our test samples at the GKSS Forschungszentrum GmbH / Geesthacht, Germany.

The principal experimental setup of this test consists of a permeate chamber and a significantly larger feed chamber. The permeate chamber and the feed chamber are connected via vents to a vacuum pump. As a result of evacuation of the permeate chamber, a gas flow through the membrane occurs. The permeation tests start when the feed side is filled with gas and the chamber is sealed off from the feed line. Permeation into the low pressure side is indicated by a pressure drop on the feed side and at the same time a pressure increase in the permeate volume.

Before each test, the apparatus was evacuated overnight, as described for the standard permeation test. The test procedure is controlled by a personal computer. A set of automatically accomplished permeation tests insured high reliability.

Detailed information concerning calculation of permeability and the experimental setup, as well as publications related to this test device are available at the GKSS Forschungszentrum GmbH⁵.

3.1.10 Mechanical tests

Mechanical properties of various samples were determined using standardised methods.

The shape of the test samples is described in EN-ISO 527-2, 1A-Type, with an overall length of 150mm, effective test length 50mm and a width of 10mm. The thickness of the samples differed from that proposed in the testing standards: the ISO standard requires samples with a thickness of 4mm. The membranes that we tested had a typical thickness in the range of 17-24µm in the case of pure polyaniline, 72-167µm for the PVDF samples, and 45-105µm in the case of PAni / PVDF composites. Before the samples were tested, they were dried overnight at 70°C and then exposed to atmospheric conditions for 6 hours.

Furthermore, the test conditions required deviations for the calculation of the e-modulus $E$: instead of the proposed tensile values at $E_1 = 0.0005\text{N/mm}^2$ and $E_2 = 0.0025\text{N/mm}^2$, we used a linear interpolation in the appropriate part of the force / elongation graph. The testing speed was 2mm/min and the detecting unit started recording at a force of 2N.
3.1.11 Sorption on polyaniline

Sorption was measured under steady-state conditions using two different, a micro force balance and a manometric test method.

3.1.11.1 Microbalance

Sorption tests were made with a micro-force balance (C.I. Electronics, Mark 2B) for pressures up to 1 bar.

The balance was kept under isothermal conditions (+/- 1°C) and the sample weight was compensated by pieces of copper counterweights.

The samples that were tested consisted of polyaniline-EB powder and polyaniline-HCL salt. The amount of polyaniline powder was 0.2-1g. The gas pressure applied to the test volume was measured with a vacuubrand DVRI pressure sensor (range 0-1.2bar) with an accuracy of 1 mbar.

Calibration was achieved with various test weights that were in the range of the expected mass uptake. To allow the electronics to reach normal operation conditions and to get constant temperature, the balance was switched on one hour before the sorption tests began.

Before each test run, the microbalance was evacuated to $10^{-3}$ mbar for several hours. When gas is applied to the polymer, the amount of sorbed molecules is indicated by an increase of weight. The sorption equilibrium for oxygen and nitrogen (indicated by no further mass uptake) was reached after approximately one to two hours. The sorption of CO$_2$ on polyaniline occurred much faster and equilibrium was reached after 10 to 15 minutes.

3.1.11.2 Manometric test method

Sorption methods are described e.g. by Koros et al. The manometric method (s. Figure II-4) mainly works with two test volumes made of steel. One volume is the storage volume for the test gas and the other volume contains the sample. The sorption of gases on polyaniline powder is indicated by the difference between the amount of gas released from volume 1 ($V_1$) into the sample volume 2 ($V_2$). The amount of non-sorbed gas in volume 2 is indicated by a pressure sensor.

First sample volume 2 was evacuated to $10^{-4}$ mbar. Then gas was gently dosed via a vent from gas reservoir $V_1$ into the sample volume $V_2$.

The experimental setup allows sorption tests at pressures up to 70 bar. The calibrated pressure indicators used were DRUCK PDCR 910, 0-135 bar, with an accuracy of at least 10 mbar.
Experimental Methods

Carbon dioxide was injected into the test cell by means of a syringe pump (ISCO Model 260D, Syringe Pump, Pump Controller, accuracy 0.01 ml) which insured constant pressure conditions and accurate dosage of liquids.

![Figure II-4: Schematic setup of sorption cell](image)

Leak tests were conducted with helium at 80 bar. The pressure drop caused by leaks was less than 2 mbar/h. The volumes were determined by injection of an incompressible liquid. With the knowledge of the density of the liquid at the given temperature, the volumes were calculated. To get accurate results, also each pressure sensor had also been calibrated before the tests started. Usually, the sorption tests started after evacuation the sorption cell for at least 5 hours at 10^{-3} mbar. From the following formulas the amount of sorbed gas can be calculated:

\[ \text{The pressure in volumes } V_1 \text{ and } V_2 \text{ can be expressed as a function of the molar amount of gas,} \]
\[ p_{(\text{ sorption cell, supply volume})} = f(n) \]
\[ \text{and can be calculated with the van der Waals equation:} \]
\[ p = \frac{n \cdot R \cdot T}{V - n \cdot b} - \frac{a \cdot n^2}{V^2} \]  
\[ \text{[II-4]} \]

with van der Waals coefficients \( a \) and \( b \) listed in Table 1, and the coefficients

\( n \) molar amount (mol)
\( p \) pressure (Pa)
\( V \) gas volume (cm³)

The measured test volumes were
\( V_1 \) (sorption cell) = 128 cm³ (minus sample volume) and
\( V_2 \) (supply volume) = 509 cm³.
Experimental Methods

Table II-1: Van der Waals coefficients

<table>
<thead>
<tr>
<th>Gas</th>
<th>van der Waals coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a (dm$^6$-bar / mol$^2$)</td>
</tr>
<tr>
<td>N$_2$</td>
<td>1.408</td>
</tr>
<tr>
<td>O$_2$</td>
<td>1.378</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>3.640</td>
</tr>
</tbody>
</table>

The absolute amount of sorbed gas was then calculated by the difference

$$\Delta n V_{\text{supply volume}} - \Delta n V_{\text{sorption cell}},$$

where $\Delta n_{\text{supply}}$ is calculated from the pressure difference between the supply volume $V_{\text{supply}}$ and $\Delta n_{\text{cell}}$ in $V_{\text{cell}}$, the sorption cell.

The function $n = f(p)$ allows the determination of the amount of gases on the basis of the pressures measured in the test volumes. Since the van der Waals equation (cf. eq. II-4) cannot be solved for $n$ the data was approximated with potential regression. The use of the regression equation is required in order to calculate the amount of gas that has left the supply volume at high pressure. To take account of non-ideal behaviour, also a potential regression was used to calculate $n$ from the pressure indicated by the pressure sensors.

In the case of CO$_2$, the liquid was dosed by a syringe pump which ensured a constant pressure (80 bar, 273 K). With the knowledge of pressure, density and the ambient temperature, the amount of gas released into the test volume could be calculated. The physical data were obtained from P. Span et al.$^8$

In the case of oxygen and nitrogen, the amount of gas was calculated with the van der Waals equation, and the correspondence between calculated data and experimental data was checked against with data from the Dortmunder Data Base for Chemical Engineering (DDB 2001) and found to be in excess of 99.8% absolute. The (sorbed) volume at STP, $V_0$, was calculated according to the formula

$$V_0 = \frac{n \cdot R \cdot T_0}{p_0}$$

with

- $p_0$: pressure under STP conditions (Pa)
- $T_0$: temperature under STP conditions (K)

and sorption $S$ was calculated by relating $V_0$ to the volume of the polymer, $V_{\text{polymer}}$:

$$S = \frac{V_0}{V_{\text{polymer}}}$$

(\text{cm}^3_{\text{STP/cm}^3_{\text{polymer}}})
Experimental Methods

3.2 Synthesis and processing of polyaniline

3.2.1 Synthesis of polyaniline

In general, the polyaniline used for the present work was obtained from ORMECON. Nevertheless, during the course of work, the interest in the route of polyaniline synthesis grew as that allows to get a deeper insight into the chemistry of this polymer and to learn how to handle and process polyaniline. It might also be important to have an alternative source for the polymer for comparison reasons. The chosen polymerisation route was in accordance with a patent published by the company Zipperling Kessler&Co.\(^9\). Compared to other routes of synthesis proposed by Chiang et al.\(^{10}\) and Rao et al.\(^{11}\), the chosen method turned out to be efficient regarding ease of operation and yield of polymer.

It must be noted that small differences in the route of synthesis may result in differences of the polymerisation rate, the molecular weight, substitution of side groups, and yield of the desired polymerisation product, desired. E.g. the introduction of side chains and/or the addition of various (polymeric) dopants have effects on dispersability and processability\(^{12,13,14}\).

Table II- 2: Agents used for synthesis of polyaniline, their molecular weight and boiling- or melting points.

<table>
<thead>
<tr>
<th>Aniline</th>
<th>M(_w): 93.12</th>
<th>T(_b): 70°C (28hPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-toluene sulfonic acid</td>
<td>M(_w): 172.21</td>
<td>T(_b): 140°C (26hPa)</td>
</tr>
<tr>
<td>Methanol</td>
<td>M(_w): 32.04</td>
<td>T(_b): 64.05 °C (1013 hPa)</td>
</tr>
<tr>
<td>Ammonium peroxydisulfate</td>
<td>M(_w): 228.2</td>
<td>T(_b): 120°C</td>
</tr>
</tbody>
</table>

- Procedure

Aniline was obtained from BASF, p-toluene sulfonic acid (p-TSA) and ammonium peroxydisulfate from Merck. The aniline was distilled before use. The other agents could be used as delivered.
A 1-liter Erlenmeyer flask is filled with aniline (0.4 mol; 37.2 g). After this a second Erlenmeyer flask is filled with p-TSA (0.5 mol, 89 g), dissolved in 500 ml of distilled water. The pH is considered to be about 1.

In a three-necked flask, 350 ml of the aqueous 1M p-TSA solution are added to the aniline. The solution is stirred well to enable good dispersion. After a few seconds, the change of colour from almost transparent to white indicates the formation of an emulsion.

The remaining 150 ml of the p-TSA are added to 0.25 mol (57 g) of ammonium peroxydisulfate. Stirring thoroughly is important to obtain complete dissolution of the oxidant.

Both solutions are then cooled down to approximately 0°C in an ice bath before the polymerisation reaction is started.

After both solutions have been cooled down to the desired temperature, the oxidant solution is added slowly, within about one hour, from a dropping funnel into the monomer solution. The beginning polymerisation is indicated by a change of emulsion colour from white to green. The progress of the polymerisation reaction is indicated by an increase of temperature and the precipitation of the polymerisation product.

The main reaction is shown schematically in Figure 11-5:

\[
\text{NH}_2 \xrightarrow{\text{oxidation}} \text{H}^+\text{A}^-; (\text{NH}_4)_2\text{S}_2\text{O}_8 \rightarrow (\text{H}^+\text{A}^-)_{n^+}, \text{A}^-
\]

Figure 11-5: Reaction scheme of polymerisation route of aniline

After complete addition of the oxidant, the reacting mixture remains in the flask for one more hour to complete the reaction. When the polymerisation has finished, the mixture is filtered to separate side products and oligomers from the polyaniline.

The final reaction product has a dark-green colour. The remaining residue is washed with 500 ml of demineralized water, 300 ml of methanol, and again with half a litre of water. This procedure may be repeated until the washing solution is colourless.

After washing, the polyaniline is dried at 50°C in a vacuum oven for 10 hours and then kept in a desiccator at room temperature.

The yield of polyaniline salt is about 40-50% by weight of the aniline used.

If required, the polyaniline salt can be deprotonated to obtain the non-doped emeraldine base. This is accomplished by dedoping in an excess of ammonia water (e.g. 500 ml 1M NH₄OH for
Experimental Methods

10g of polyaniline salt) for 12 hours. After ion exchange has completed, the emeraldine base is washed several times with demineralized water and is dried again.

3.2.2 Dispersion of emeraldine base

Polyaniline can only be processed by means of dispersion. A suitable dispersion agent for emeraldine base is NMP. Before dispersion, the polymer has to be essentially water-free. This is achieved by drying it for several days at 50°C and keeping the polymer in a vacuum. During the drying process, agglomerates often are formed. For this reason further processing requires pulverisation either by means of pestle and mortar or other mechanical grinding devices.

The dispersion of polyaniline in the solvent occurs under constant stirring. The polymer is added slowly to the solvent, approximately 2-5g per litre of solvent. After addition of the powder, stirring continues for half an hour. In case of coagulation or precipitation of insoluble particles, the dispersion can be homogenised by means of ultrasonic treatment or the use of a high speed mixer.

Indispersible particles are then filtered from the dispersion by at least 2-3 successive filtration steps through filter paper. The dispersion is now readily prepared and can be used for further processing steps.

3.2.3 Production of unsupported polyaniline membranes

Polyaniline films were produced by means of solution casting: the dispersion was spread onto glass plates followed by evaporation of the solvent.

In order to get defect-free and stable films the glass plate has to be prepared carefully to avoid inhomogenities of the polyaniline film: the substrate must be cleaned thoroughly from all dust and without scratches.

The glass plate was washed with soap, rinsed with demineralized water and ethanol before being coated. After that the glass plate was dried at 125°C for two hours.

A reproducible and even quality of films can be obtained if the NMP is evaporated in a drying cupboard for two hours at 125°C. That way it is possible to create defect-free films with an area up to 18x24cm and a thickness of 5 to 80µm, depending on the amount or concentration of the dispersion (cf. Table II-3).

Mechanically rather robust polyaniline membranes are separated from the glass plate by immersion into water. The as-cast membranes have a copper-like colour. The thicker membranes
Experimental Methods

(more than 20µm) were produced by spreading out the dispersion on the polyaniline coated glass plate followed by curing a second time.

It is not possible to produce self-supporting films from ORMECON polyaniline (emeraldine salt, doped with p-TSA) dispersions. Independent of their thickness, these films decompose during immersion into water.

To get the highest reproducibility possible, the films were made of emeraldine base (0.5% EB, dispersed in NMP) produced by ORMECON.

Table II-3: Amount of dispersion to get films with different thicknesses

<table>
<thead>
<tr>
<th>V Dispersion / ml</th>
<th>100</th>
<th>50</th>
<th>25</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average film thickness / µm</td>
<td>18-22</td>
<td>8-10</td>
<td>4-5</td>
<td>2-3</td>
</tr>
</tbody>
</table>

3.2.4 Production of polyaniline-based composite membranes

Composite membranes were produced by using a new production technique: solution casting of polymeric support materials on top of polyaniline films.

- Procedure

The concentration of the polyaniline dispersion used is approximately 0.5wt-% polyaniline in NMP. About 0.1ml of dispersion per cm² substrate is required to create a film 3-4µm thick. The polyaniline film was obtained when the NMP was evaporated in a drying cabinet for 2 hours at 125°C.

The copper-coloured polyaniline film was now ready to be coated with polymeric materials. A certain amount of a polymer solution (3wt-%) was dissolved in an NMP / DMSO (3:1) mixture to create such a composite membrane. This mixture was poured onto the prepared polyaniline film which was still placed on the glass substrate. To stabilise a prepared polyaniline film of 100cm² in this way, 20-25ml of the solution were used.

The polyaniline / composite membrane was dried again at 60°C for several hours, until the solvent had evaporated. During the evaporation process a spongeous support film forms and combines with the polyaniline film. Thus the polymeric support materials create a stable and spongeous carrier structure which can be passed by gases with negligible resistance.

Finally, the composite membrane was separated from the substrate by immersing the coated glass plate into a (1:1) mixture of n-propanol and demineralized water for several hours.
3.2.5 Doping of polyaniline membranes

Doping from aqueous solutions is easy to control, requires little equipment, and is well established.

The membranes made according to the recipe described above were doped (i.e. protonated) by immersion into hydrochloric acid (4M), dedoped by similar treatment with ammonia liquor (1M) and slightly redoped with a 1.75·10⁻² molar HCl solution\(^{15,16}\). The extent of doping can be varied between 0% (completely undoped) up to 50% of the monomer units (completely doped) by varying the concentration of the dopant used\(^{17}\).

Usually a basin was filled with the required doping (or dedoping) agent and the polyaniline film was immersed into the liquor. In order to ensure doping to saturation, treatment with an excess amount of solution is required. A typical sample (e.g. 5×5cm, thickness 5-15 µm) was treated with 250ml of acid or base. In the case of doping with 1.75·10⁻² molar hydrochloric acid, a larger excess of solution, one litre, was used.

The membranes were stored for 24 hours in the solution, and in the case of treatment with diluted HCl for two days, so that saturation doping occurred.

Doping experiments can also be performed by doping from the gas phase. To do this the samples were exposed to HCl gas in a reservoir for a certain period of time\(^{18}\). In the present work gas phase doping was only used for some special tests (see IV-8.1).

After the doping treatment, the membranes were allowed to dry for several hours at 60°C in the vacuum oven and stored in a desiccator.

The as-cast and dedoped membranes can easily be identified: the non-doped membranes have a copper-like colour, whereas the doped membranes appear green-blue.

To confirm the required doping state and the exchange rates, the samples were tested with a standardised photometric chloride test (Merck).

Table II- 4: Acid and base treatment of polyaniline membranes

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Doping / HCl 4M</th>
<th>Dedoping / NH₄OH 1M</th>
<th>Redoping / HCl 0.0175M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time/ hours</td>
<td>24</td>
<td>24</td>
<td>48</td>
</tr>
<tr>
<td>Exchange rate / %</td>
<td>48</td>
<td>2</td>
<td>20</td>
</tr>
</tbody>
</table>


3.2.6 Coating of membranes with polyorganosiloxanes

To prevent microporous defects, membranes can be treated with agents that plug inherent pores. In this work, commercially available organosiloxanes were polymerised on top of the polyaniline layer to seal the surface.

The organosiloxane used was *Dehesive 930* (Wacker Chemie, Germany).

In 100g of isoctane, 3g of Dehesive, 1g of catalyst-oil, and 0.15g of netting agent were dissolved under constant stirring. The coating mixture was then stirred overnight.

In order to combine the polyorganosiloxane with the polyaniline layer, the membrane was immersed for at least 3-5 times into the coating solution.

The evaporation of the solvent (at 50°C for 1 hour) leads to polymerisation of the organosiloxane in a way that pores are plugged and the polyaniline surface is sealed from influences of the environment.
Literature PART II


5. GKSS Forschungszentrum GmbH, 21494 Geesthacht, Germany, Publication Carsten Hasler "Automatisierte Permeabilitätsmessung für Einzelgase", Institut für Chemie


16. R.B. Kaner, R. Anderson, B.R. Mattes, and H. Reiss, United States Patent Number 5096586, Table 2

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4 Characterisation and Results

4.1 Synthesis and dispersion of polyaniline

A large number of publications about polymerisation procedures\textsuperscript{1,2,3,4} are incomplete with regard to details of the polymerisation reaction and process parameters. However, in the dissertation by F.A. Lux\textsuperscript{5} and the publication of Wessling \textit{et al.}\textsuperscript{6}, several synthesis routes are proposed and the polymerisation process is described in great detail.

The synthesis approach in this work (see Chapter II-3.2.1) is based on the above synthesis routes and was adapted to the requirements of lab-scale production.

For acidification e.g. hydrochloric acid (HCl), sulphuric acid (H\textsubscript{2}SO\textsubscript{4}) or p-toluenesulfonic acid (p-TSA) can be used. The oxidant for all polymerisations was ammonium peroxydisulfate. It turned out that the yield of polymer directly depends on the adjustment of parameters such as:

- time used for addition of the oxidant (20-30 minutes)
- stirrer rotation (> 1 /s)
- amount of aniline (20-80g per batch)
- choice and concentration of acid (0.5-2M)
- reaction temperature (0-5°C)

When staying within these boundary conditions it is possible to increase the yield of polyaniline by up to 50\% by weight of aniline used under the set of conditions as described in Chapter 3.2.1. Ion exchange as well as drying of the polymer are required for further processing.

Dispersing of polyaniline in NMP is one major task. If samples have been insufficiently prepared, polyaniline may precipitate from the solvent. There can be various reasons for that:

- incomplete ion exchange
- insufficient washing
- residual water in polymer
- the use of agglomerated powder

Homogenisation of the mixture is quite important in order to minimise the loss of polymer (once agglomerated and precipitated in NMP, the polymer cannot be dispersed again). Careful filtration is also important, because small particles often cause cracks and pinholes in polyaniline membranes.
Characterisation and Results

In order to avoid agglomeration and precipitation of particles, the following operations are necessary:

- complete deprotonation of polyaniline
- use of essentially dry polymer
- homogenisation
- filtration

4.2 Production of polyaniline films and composite membranes

Poor mechanical properties of self-supporting polyaniline films\(^7\) and the low permeability of pure polyaniline membranes lower possibilities for industrial applications. Many publications\(^1\)\(^4\)\(^7\) report on pure polyaniline membranes with a thickness in the range between 10 to 100µm. Kuwabata et al.\(^2\) argue that it might not be possible to create defect-free self-supporting films thinner than 20µm. They also show that defect-free thin polyaniline / alumina composites can be produced one order of magnitude thinner. Defects on the surface of the support material require polyaniline layers of more than 3µm to bridge those defects. In order to produce the required thin and gas-selective polyaniline layer, a porous support might be coated. As polyaniline is neither soluble nor meltable there are many restrictions regarding possibilities to handle it. Polyaniline dispersed in NMP is the only point to start processing the polymer. Because of this restriction, coating of support materials causes a number of problems and often does not result in dense and stable top layers:

- fused materials often tend to decompose during drying or doping processes
- suitable support materials are severely affected by NMP
- undesired doping of polyaniline occurs due to acid groups in the support material
- precipitation of polyaniline particles on substrate surface, caused by interactions of polyaniline with dissolved support compounds
- swelling, shrinking, or deformation of support materials by solvent effects
- the temper process often affects the support and the layer. Shrinking and different evaporation times of the solvents must be considered
- no film formation occurs because surface materials are not wettable
- embrittlement of support and polyaniline layer caused by drying process
Table III-1: Coating properties of typical membrane materials; + good, 0 medium, - bad.

<table>
<thead>
<tr>
<th>Coated Material</th>
<th>Wettability</th>
<th>Resistance to NMP</th>
<th>PANi film formation</th>
<th>Deformation after drying</th>
<th>Dense PANi layers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polycarbonate</td>
<td>+</td>
<td>0</td>
<td>0</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Polyamide</td>
<td>+</td>
<td>0</td>
<td>0</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Nafion®</td>
<td>+</td>
<td>0</td>
<td>0</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>PDMS</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cellulose acetate</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>PAN</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Ethylcellulose</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>PVDF</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>PEI</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
</tbody>
</table>

Table III-1 gives an overview of experiments in which the selected polymers were coated with polyaniline dispersion. All of the listed materials could be wetted sufficiently except PDMS which on the other hand was the only material that could resist NMP. Films only formed on the materials if polycarbonate, polyamide or Nafion® were used. On none of the materials dense polyaniline layers were formed, mostly because of serious deformation of the carrier polymers that occurred during the drying process.

These observations led to the development of a new way of producing composite membranes. With the knowledge that thin polyaniline layers can be created on glass substrates, a coating of the polyaniline layer with an appropriate support polymer from the liquid phase might yield a strong composite material.

Various polymeric materials such as cellulose acetate, polyacrylonitrile, ethylcellulose, poly(vinylidene fluoride) and polyetherimide were combined with polyaniline: carrier materials that are easy to handle, easy to process, and inexpensive.

Several tests were conducted with a number of suitable support polymers, and some met the requirement of forming of thin, high-quality membranes. These requirements were:

- no shrinking and deformation during solvent evaporation
- no expansion while membrane is exposed to water
- no acid groups that affect the polyaniline
- formation of stable, flexible, and porous structure
- adhesion of support layer to polyaniline layer
One way to increase the permeate flux through a membrane while maintaining its selectivity with regard to the permeants is to minimise the thickness of the permselective layer. The task is to obtain stable membranes that yield high selectivity and a high flux rate.

For gas permeation tests, self-supporting polyaniline films must have a thickness of at least 10-15µm.

The mechanical stability can be enhanced by fusing thin polyaniline films with suitable carrier materials. Then the thickness of the polyaniline film itself can be reduced. This was realised by the new technique mentioned, a process which consists of two successive steps. The process is described using PVDF as an example.

Since polyaniline films with perfect properties can be created on glass substrates, a strong composite material may be achieved by coating such a layer on the glass substrate with an appropriate support polymer from the liquid phase (instead of coating a carrier material with a polyaniline layer).

Such carrier materials, polymers as mentioned above, were diluted in appropriate solvents. Slow evaporation of the solvent leads to spongeous and highly porous, but mechanically stable support structures.

It was found that only PVDF tends to show the desired porosity and mechanical properties.

Even if the other materials may also be used as appropriate support materials, PVDF has some outstanding properties: this polymer does not fuse with polyaniline, but still makes a stable entity with it (cf. Figure III-17 and III-18). In contrast to the other materials PVDF is comparatively flexible after having been dried. None of the other composite membranes could be made sufficiently large and defect-free. During the first diffusion tests on the composite materials it soon turned out that only PVDF composites were not damaged during installation into the diffusion apparatus.

If required, the support can be separated from the polyaniline layer, e.g. by treatment with hot water. Since the support has a negligible resistance to the permeating gas, the permeation properties only depend on the polyaniline layer. For permeation studies, composite films with an effective polyaniline thickness of as little as 1.6µm were produced.

The difficulty to produce thin, stable, and defect-free polyaniline films is illustrated in Table III-2 which shows a list of authors and the corresponding film thicknesses that were tested. While self-supporting films are in a range of 10-100µm, only supported polyaniline films thinner than 10µm are shown.
### Table III-2: Thicknesses of polyaniline films used for gas permeation tests

<table>
<thead>
<tr>
<th>Publication, author</th>
<th>Thickness of PANi film/µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chang <em>et al.</em></td>
<td>100</td>
</tr>
<tr>
<td>Conklin <em>et al.</em></td>
<td>50</td>
</tr>
<tr>
<td>Hachisuka <em>et al.</em></td>
<td>20-30</td>
</tr>
<tr>
<td>Rebattet <em>et al.</em></td>
<td>10-15</td>
</tr>
<tr>
<td>Lee <em>et al.</em></td>
<td>5</td>
</tr>
<tr>
<td>Kuwabata <em>et al.</em></td>
<td>20-30</td>
</tr>
<tr>
<td>Kuwabata <em>et al.</em></td>
<td>3-4</td>
</tr>
<tr>
<td><strong>Present work</strong></td>
<td></td>
</tr>
<tr>
<td>Self-supporting films</td>
<td>10 - 70</td>
</tr>
<tr>
<td>PANi / PVDF composite</td>
<td>1.6 - 8.4</td>
</tr>
</tbody>
</table>

### 4.3 UV-Vis Spectra

Figures III-1 and III-2 show typical UV-Vis spectra for polyaniline base and polyaniline salt. It can be seen that doping of the emeraldine base results in a change of colour from blue to green.

![UV-Vis Spectra of polyaniline base](image_url)

The absorption spectra help to determine the doping state of the polymer. In the visible range, polyaniline base shows two absorption peaks. The maximum located at approximately 320nm is explained with the $\pi-\pi^*$ transition of a benzenoid amine structure, whereas the second peak at 620nm is due to a quinoid structure\(^{11,12}\) (cf. Figure III-1).
Characterisation and Results

Doping of the film decreases the absorption at 320nm, and a third absorption peak with less intensity appears around 420nm. At the same time doping shifts the second broad absorption maximum from the visible band (620nm) into the near infrared area (> 900nm), which indicates the formation of the polaron band which is due to the delocalisation of the radical cation$^{13}$.

Figure III-2: UV-Vis spectra of polyaniline-HCl salt
4.4 ATR-IR examinations

Figure III-3 shows the ATR-IR (attenuated total reflection infrared) spectrum of polyaniline films in the as-cast state and in the fully doped (HCl) state.

Figure III-3: IR-spectra of polyaniline salt and polyaniline base

The upper dashed line represents the absorbance of polyaniline base, and the graph below was obtained from the doped state. The undoped and the doped films show a number of significant peaks in the range of 500 to 4000 cm\(^{-1}\).

An interpretation of the spectra for emeraldine base and the corresponding HCl salt is given in Tables III-3 and III-4 where the absorbance peaks are related to the corresponding bonding modes.

Except for small differences, the peaks for polyaniline base and salt appear in the same region. The strong band at 1150 cm\(^{-1}\) in the base is broader and much more intense than in the salt spectrum. Doping of polyaniline leads to \(\text{NH}_2^+\) groups, which can be observed at 710 cm\(^{-1}\). At 1305 cm\(^{-1}\) a new peak appears, indicating the protonation of nitrogen. A residue of NMP is indicated by the peak at 1700 cm\(^{-1}\), which was also found by Lux\(^5\). This spectrum is comparable to those obtained by Rao et al.\(^{14}\) and Chang et al.\(^3\).
**Characterisation and Results**

Table III-3: ATR-IR absorption maxima ($\lambda_{\text{max}}$) of polyaniline base

<table>
<thead>
<tr>
<th>Wave number / cm$^{-1}$</th>
<th>Functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>3250</td>
<td>N-H stretching</td>
</tr>
<tr>
<td>3050</td>
<td>C-H stretching</td>
</tr>
<tr>
<td>1700</td>
<td>C=O, residue of NMP</td>
</tr>
<tr>
<td>1660</td>
<td>NH$_2$</td>
</tr>
<tr>
<td>1581</td>
<td>C-C ring stretching vibrations of quinoid and benzoid rings</td>
</tr>
<tr>
<td>1487</td>
<td>C-C ring stretching vibrations of quinoid and benzoid rings</td>
</tr>
<tr>
<td>1378</td>
<td>C-C ring stretching vibrations of quinoid and benzoid rings</td>
</tr>
<tr>
<td>1292</td>
<td>C-N-C bending</td>
</tr>
<tr>
<td>1220</td>
<td>N-H or C-C symmetric component of stretching mode</td>
</tr>
<tr>
<td>1146</td>
<td>C-H in-plane and out-of-plane stretching mode</td>
</tr>
<tr>
<td>820</td>
<td>C-H in-plane and out-of-plane stretching mode</td>
</tr>
</tbody>
</table>

Table III-4: ATR-IR absorption maxima ($\lambda_{\text{max}}$) of polyaniline (HCl) salt

<table>
<thead>
<tr>
<th>Wave number / cm$^{-1}$</th>
<th>Functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>3246</td>
<td>N-H$_3$ stretching mode</td>
</tr>
<tr>
<td>1660</td>
<td>NH$_2^+$</td>
</tr>
<tr>
<td>1612</td>
<td>N-H$_3$ bending vibration</td>
</tr>
<tr>
<td>1555</td>
<td>C-C ring stretching vibrations of quinoid and benzoid rings</td>
</tr>
<tr>
<td>1461</td>
<td>C-C ring stretching vibrations of quinoid and benzoid rings</td>
</tr>
<tr>
<td>1370</td>
<td>C-C ring stretching vibrations of quinoid and benzoid rings</td>
</tr>
<tr>
<td>1305</td>
<td>C-N$^+$-C bending</td>
</tr>
<tr>
<td>1254</td>
<td>C-N$^+$-C bending</td>
</tr>
<tr>
<td>1175</td>
<td>C-H in-plane and out-of-plane stretching mode</td>
</tr>
<tr>
<td>800</td>
<td>C-H in-plane and out-of-plane stretching mode</td>
</tr>
<tr>
<td>710</td>
<td>NH$_2^+$ wagging</td>
</tr>
</tbody>
</table>
4.5 MALDI-TOF examinations

Figures III-4 and III-5 show MALDI-MS (Matrix Supported Laser Desorption / Ionisation Mass Spectroscopy) spectra of polyaniline base.

![MALDI-MS spectra of polyaniline base](image)

Figure III-4: Examination of the polymerisation rate of polyaniline with MALDI-MS, m/z range = 0-2800

Organic molecules and fragments of these can be released out of a silicon-based matrix by irradiation with a pulsed laser beam. MALDI-MS can identify molecules > 200u (atomic mass unit, 1u = 1,660531 \cdot 10^{-27} \text{ kg}).

The mass range examined was 0-2800u (cf. Figure III-4). The high resolution plot (cf. Figure III-5, inset) shows that each of the peaks is sub-divided into smaller peaks, which result from isotopes of carbon.

The main peaks between 300 and 1500u provide evidence that polyaniline is within this mass range, but does not explicitly point out a polymer distribution. By using photoionisation mass spectroscopy techniques, Sauerland et al.\textsuperscript{15} showed that polyaniline chains consist of C\textsubscript{6}H\textsubscript{4}NH (91u) and C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2}\textsuperscript{+} units (93u). The mass range they examined was up to 1000u. These results indicate that the fragments of chemically synthesised polyaniline are based on polyaniline oligomers with different quantities of C\textsubscript{6}H\textsubscript{4}NH and C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2}\textsuperscript{+} units.

Figure III-5 shows a magnification of the mass range 900 to 2500u. Repeating signals from 1300 to 2350u indicate a polymer distribution.
Characterisation and Results

The expected differences of weight are in the mass range of fragments that are assigned to aniline (91 or 93u), whereas the detected polymer fragments differ by 74u. The question arises to which kind of fragments this set of signals belongs to. One explanation may be found in a statement in the dissertation of F.A. Lux. Some side reactions during polyaniline polymerisation may lead to substitution of hydrogen (at the quinoid ring) by aniline radical cations. Supposedly this leads to the formation of substituted phenylquinineimines so that the molecular weight of 74u might be assigned to a benzene fragment.

Because of the mass range in the spectra shown, a polymerisation rate of polyaniline in a range of 4 to 16 may be assumed. This is quite a remarkable result, because earlier publications by Hachisuka et al. claimed average molecular weights of $1.6 \times 10^5$u, determined by means of gel permeation chromatography and also MacDiarmid et al. also reported on fractions with molecular weights in a range of 22,000 to 380,000u.

The differences between the latter result and those in this work are very large. This raises the question if either the polymerisation routes may have caused obvious differences in chain lengths, or perhaps different analysis techniques.

Where mass spectroscopy directly indicates the overall mass range of the sample and its (polymeric) fragments, GPC studies give information about the affinity of the sample to the gel matrix. It has not been pointed out so far that the fractions may consist of several short polymer chains that form loops and agglomerations which are caused by intermolecular interactions.

![Figure III-5: Examination the polymerisation rate of polyaniline with MALDI-MS, m/z range = 900-2600](image-url)
4.6 BET examinations of polyaniline powders and films

BET analysis was performed to obtain information on the specific surface area of polyaniline powder and polyaniline films. The adsorbent is nitrogen and the results were calculated according to the BET sorption model. Table III-5 gives an overview of the surface areas found.

Table III-5: Specific surfaces for various states of polyaniline

<table>
<thead>
<tr>
<th>Material</th>
<th>BET surface / m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>As synthesised powder (p-TSA)</td>
<td>11.64</td>
</tr>
<tr>
<td>Doped powder (HCl)</td>
<td>18.95</td>
</tr>
<tr>
<td>Dedoped powder</td>
<td>18.70</td>
</tr>
<tr>
<td>Partially redoped powder (HCl)</td>
<td>18.86</td>
</tr>
<tr>
<td>As-cast film</td>
<td>0.037</td>
</tr>
<tr>
<td>Partially redoped film (HCl)</td>
<td>1.084</td>
</tr>
</tbody>
</table>

Neither the films nor the powders show sorption isotherms which are typical for porous materials. The measured BET areas for the powders are much bigger, compared to those of the films. The as synthesised state (doped with p-TSA) has the smallest specific surface area (11.64 m²/g) of the powders, whereas the specific surface area of the other exchange states (doped, dedoped and redoped) is slightly bigger (18.7-18.95 m²/g). The results compare favourably with the results obtained by Wessling et al.\textsuperscript{17} who reported on specific surface areas of < 15 m²/g for polyaniline powder.

Figure III-6: Typical sorption isotherm for BET analysis on polyaniline
Characterisation and Results

The BET plot shown in Figure III-6 is typical for substances which do not show any intrinsic porosity. This implies that only the geometric surface of the polymer particles can be determined.

The as-synthesised polyaniline (p-TSA doped) shows a slightly smaller specific surface area than the HCl-doped polymer. It cannot be excluded that the choice of doping agent (p-TSA vs. HCl) is responsible for the difference.

As for the powders, also for the film samples no porosity can be derived from the shape of the adsorption isotherms: typical sorption isotherms for porous materials have a "hysteresis loop", a gap between the adsorption and desorption isotherm, which is attributed to capillary condensation taking place in the mesopores.

The specific surface area of the redoped sample was significantly larger than the surface area of the as-cast membrane. According to Anderson et al. doping and dedoping polyaniline results in an increase of pathways in molecular dimensions. The increase of free volume within the polymer in combination with the introduction of various anions is made responsible for outstanding selectivity with respect to gas separation.

An increased number of surficially accessible pores might be responsible for the larger specific surface area, but the present results only give restricted evidence as to porosity. It might also be possible that sorption increases because of surface effects caused by the dopant. It also has to be mentioned that the redoped membrane was extremely brittle so that the sample consisted of a number of pieces. This may also have had an influence on the measurements.

However, compared with the powders, the films have a much smaller surface area. From the present BET results, a doping/dedoping-induced increase of porosity cannot be substantiated.

4.7 Specific conductivity

The degree of doping can be estimated by determining the specific conductivity of the material. In order to get highly reproducible data, conductivity was determined by means of the four-contact-point methods according to van der Pauw and ISO 1853.

The difference between the doped and the dedoped state clearly shows the transition from the isolator state to the conducting state of polyaniline.

With a specific resistance of > 2000000(Ω-cm)^{-1}, the as-cast membrane is an insulator, whereas the doped sample with a conductivity of 1 S/cm is a conductor. The dedoped state has a significantly lower conductivity than the as-cast exchange state (cf. Table III-6).
Table III-6: DC-conductivity of different states of polyaniline in S/cm

<table>
<thead>
<tr>
<th>Exchange state</th>
<th>v.d. Pauw / S/cm</th>
<th>ISO 1835 / S/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-cast</td>
<td>&lt; 5·10⁻⁷</td>
<td>&lt; 5·10⁻⁷</td>
</tr>
<tr>
<td>Doped</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Undoped</td>
<td>3·10⁻⁴</td>
<td>3·3·10⁻⁴</td>
</tr>
<tr>
<td>Redoped</td>
<td>1.47·10⁻²</td>
<td>2.17·10⁻²</td>
</tr>
</tbody>
</table>

The conductivity measured indicates that the dedoping process is incomplete, or that some ionic components on the surface cause a little conductivity. The redoped membrane has a conductivity between the as-cast and the doped state.

4.8 Contents of water

Figure III-7 gives an overview of the amount of moisture in polyaniline powders and films that have been stored under defined conditions (60-65% relative humidity at 20-22°C).

Approximately 5-15wt-% of volatile compounds are contained in the polyaniline. In the case of polyaniline (HCl) powder, the doped state releases a significantly higher amount of volatiles (> 15wt-%) than the undoped exchange states, which exhibit a weight loss of between 5 to 10wt-%. The weight loss of the redoped state was found to be of 11wt-%.
Characterisation and Results

It appears that the affinity towards water (coming from humidity of the air) is given by the concentration of chloride in the polymer. In the case of the as-synthesised powder, the dopant is p-TSA. This may have an effect on the affinity of water to polyaniline.

4.9 Specific gravity

Figure III-8 presents the specific gravity of various polyaniline samples. The specific gravity of all samples is between 1.35 and 1.45 g/cm$^3$.

![Figure III-8: Specific mass of various polyaniline samples](image)

The highest specific gravity was measured for the doped samples (1.45 g/cm$^3$) due to the chloride content, whereas the undoped samples have a density slightly below that (1.35 g/cm$^3$). The redoped samples have a similar density compared to the dedoped exchange state. The chart also shows no significant difference between membranes and powders. Commercially available polyaniline$^{18}$ (fully doped) has a density of 1.4 g/cm$^3$, and the density for dedoped material was determined to be 1.3 g/cm$^3$.$^{19}$

Rebattet et al.$^4$ assume, that the density of polyaniline follows from a linear dependence on the doping level and estimate it to be 1.32 g/cm$^3$ in the case of the redoped powder. The values found correspond quite well with the data in the literature.
4.10 Mechanical properties

In order to assess the mechanical properties of our composite materials, the tensile properties were determined according to standardised test methods as per EN-ISO 527 (DIN 53455). Typical force vs. elongation (F-S) diagrams for the samples PANi, PANi / PVDF, and PVDF are shown in Figures III-9 to III-11.

The graphs for PVDF and PVDF / PANi (which mainly reflect the property of PVDF) show a similarity in shape and can be subdivided into three parts:

1. almost linear increase
2. increase of elongation with constant force
3. rupture of the sample

The graph for PANi differs from the other two plots, and has two significant parts:

1. a linear increase of the force vs. elongation curve
2. breaking of the sample

![Graph showing mechanical properties](image-url)
Figure III-10: Determination of tensile properties of PAni (EB) / PVDF composite according to (EN-ISO 572). Sample thickness: 84µm

Figure III-11: Determination of tensile properties of PVDF according to (EN-ISO 572). Sample thickness: 167µm
Figures III-9 - 11 show typical $F$ vs. $S$ graphs for brittle materials: small elongation, immediate rupture. The force $N$ at which the sample breaks is called tensile strain at break, $\sigma$. The samples collapse at this point, which is indicated by the sudden decline of the $F$ - $S$ curve.

Figures III-9 and III-10 also show an intermediate state which results from a wire drawing effect: increasing elongation and simultaneous increase of the sample area. It seems that the applied force is almost constant while the elongation increases.

The $E$-modulus $E$ of the PANi / PVDF composite (467N/mm²) is slightly above the value of pure PVDF (383N/mm²) and approximately three times smaller than the result for pure polyaniline (1480N/mm²).

Figures III-10 and III-11 indicate that $\sigma$, of the composite material (18.1N/mm²) is determined by the main compound, PVDF (19.4N/mm²), and it also is about three times smaller than the result for pure PANi (67.6N/mm², cf. Figure III-9).

Characteristic results of the mechanical tests are listed in Tables III-7 and III-8, with information on some selected mechanical data of various polymers for comparison.

According to these data, $\sigma$, for PVDF and PANi / PVDF samples is in the range of polystyrene with high impact strength, but significantly below the data for hard and soft PVC, whereas $\sigma$, for pure PANi films is between the values of soft and hard PVC.

The $E$-modulus of the PANi samples is almost comparable to that of conducting polymer polypyrrole, but small compared to polymers such as PVC and polystyrene.

Compared to these materials, the PVDF and PANi / PVDF composite materials have an $E$-modulus which is significantly smaller.

Table III-7: Mechanical properties of membrane materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Tensile stress at break, $\sigma$, N/mm²</th>
<th>Max. force, N</th>
<th>Max. elongation, %</th>
<th>$E$-Modulus, E/N/mm²</th>
<th>Thickness, μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF</td>
<td>19.4</td>
<td>29.1</td>
<td>11.6</td>
<td>383</td>
<td>146</td>
</tr>
<tr>
<td>PANi</td>
<td>67.6</td>
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<td>1480</td>
<td>21</td>
</tr>
<tr>
<td>PANi / PVDF</td>
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<td>13.0</td>
<td>10.7</td>
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<td>75</td>
</tr>
</tbody>
</table>
Table III-8: Mechanical properties of various polymers

<table>
<thead>
<tr>
<th>Material</th>
<th>Tensile stress at break, ( \sigma ), N/mm(^2)</th>
<th>Max. elongation/ %</th>
<th>E-Modulus E, N/mm(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polypyrrole</td>
<td>36</td>
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<td>1500</td>
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<tr>
<td>Hard-PVC</td>
<td>100</td>
<td>5</td>
<td>4000</td>
</tr>
<tr>
<td>Soft-PVC</td>
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<td>200</td>
<td>3000</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>30</td>
<td>30</td>
<td>3500</td>
</tr>
<tr>
<td>Polystyrene (high impact strength)</td>
<td>20</td>
<td>20</td>
<td>1500</td>
</tr>
</tbody>
</table>

4.11 SEM and EDX examinations

SEM micrographs were recorded of polyaniline (ES) powder and various polyaniline films to obtain information on the morphology, structure, and surface appearance of the samples.

4.11.1 Polyaniline powder

Directly after the polymerisation reaction, polyaniline is in the "as synthesised" (doped) state. The doping agent of this polyaniline modification is p-toluenesulfonic acid.

Figure III-12: Polyaniline powder, as synthesised

Figure III-12 shows a typical representative of polyaniline powder, the structure of which does not depend on the degree of doping and the kind of dopant. A magnification of 10000 times shows powder particles with a diameter of < 500nm. Smaller particle structures are beyond the resolution of the SEM.
4.11.2 As-cast and redoped polyaniline membranes

Examinations of the structure and the thickness of PANi films are of special interest for gas separation. Figures III-13 and III-14 show typical examples of self-supporting polyaniline films.

![Figure III-13: Self-supporting polyaniline (EB) membrane](image1)

The thickness of the as-cast membrane is estimated to be 25µm, and 5µm in the case of the redoped membrane. These membranes are essentially pore-free and do not show any microporous structures. For those membranes, even higher magnification does not give any evidence of specific structures that can be related to gas transport properties, except of the important information that the membrane is essentially pore-free.

![Figure III-14: Self-supporting, redoped polyaniline (ES) membrane](image2)
Membranes in other doping states do not exhibit any observable change in their morphology: Figure III-14 shows a redoped membrane. This membrane does not reveal any structure that can be related to the doping reaction. Also, further examination of dedoped and redoped membranes did not give any evidence of a change in membrane structure.

EDX examinations was performed on redoped polyaniline membranes and that proved the presence of chlorine, which is indicated by the large peak in the middle of the spectrum (cf. Figure III-15). Also, gold was detected, which was expected due to sample preparation (see Chapter III-3.1.6)

![Figure III-15: EDX spectra of HCl-doped polyaniline membrane](image)

Figure III-15: EDX spectra of HCl-doped polyaniline membrane
4.11.3 Microporous polyaniline membranes

Electron micrographs of the cross-section areas of some polyaniline membranes show small holes of approximately 0.4µm of diameter (cf. Figure III-16), whereas others (cf. Figures III-13 and III-14) appear to be free of defects.

Figure III-16: SEM micrograph of a macroporous polyaniline membrane. Evenly distributed pores with a diameter of approximately 400nm are visible and indicated by arrows.

It is not clear what may have caused the observed macropores (diameter > 50nm), however, it is evident that these membranes will have separation factors in conformity with Knudsen diffusion (see Chapter I-2.1.3). The presence of such pores has not been observed before. Other researchers have mentioned porosity in the case of very thin films without pointing out the origin of these defects.

It is possible that the drying process is responsible for the formation of these pores. Longer evaporation times might reduce the defect concentration. It could also be possible that impurities in the dispersion (or micro-agglomeration of the polyaniline dispersion) are responsible for the defects.
4.11.4 Polyaniline composite membranes

SEM examination was performed to investigate various polymeric materials that had been combined with polyaniline, such as cellulose acetate, ethyl cellulose, polyvinylidene fluoride and polyetherimide. It is of particular interest to get an insight into the morphology of the composite materials, especially the morphology of the carrier materials.

4.11.4.1 Polyaniline / PVDF composites

Figures III-17 and III-18 show cross sections of polyaniline / PVDF composite membranes.

![Figure III-17: Polyaniline / PVDF composite membrane](image)

The evenly formed polyaniline layer can clearly be discerned from the porous support structure. The morphology of the PVDF carrier has an appearance similar to the structure of sintered plastic or metal particles.

![Figure III-18: Cross section of a polyaniline layer on a spongy PVDF support](image)
4.11.4.2 Polyaniline / PVDF / POS composites

Figure III-19 shows a polyaniline / PVDF composite membrane that is coated with polyorganosiloxane (POS). As in micrographs III-17 and III-18, the PVDF support structure can be identified clearly, as well as the polyaniline layer on top of the support. The sealing material POS that covers the upper side of the membrane adheres tightly to the polyaniline.

Figure III-19: Structure of composite membrane consisting of PVDF and polyaniline, coated with polyorganosiloxane, magnification 1500 times

Figure III-20 shows a defect of the POS layer that was caused by mechanical impact of a pointed object. The siloxane layer itself does not have an inherent structure, but its surface has a wavy appearance. Those structures are typically formed by convective air flow during solvent evaporation in the drying cabinet.
Characterisation and Results

As expected the EDX micrograph in Figure III-21 gives evidence of the presence of silicon in the POS layer, indicated by the marked peak in the spectrum.

Figure III-20: Polyorganosiloxane coating on polyaniline

Figure III-21: EDX spectrum of polyaniline membrane, coated with polyorganosiloxane
4.11.4.3 Polyaniline combined with various support polymers

Besides composites with PVDF, also composite membranes consisting of celluloseacetate, ethylcellulose, poly(vinylidenfluoride) and polyetherimide were produced.

All support structures that were examined in this work are characterised by high porosity. However, some of the materials tend to form asymmetric structures with less porous morphology in the direction towards the polyaniline layer. This can be seen in the case of composites consisting of ethylcellulose (cf. Figure III-22).

In contrast to the other support materials that appear to be much more homogeneous with evenly distributed cavities.

Figure III-22: Polyaniline / ethylcellulose composite membrane

Figure III-23: Polyaniline / polyetherimide composite membrane
Adhesion of the polyaniline to the support varies. E.g. for the combination of polyaniline with ethylcellulose, a transition from one material to the other is difficult to observe (cf. Figure III-24). However, in the case of polyaniline combined with polyetherimide, the layers are even partially separated by a small gap (cf. Figure III-23).

Figure III-24: Polyaniline / cellulose acetate composite membrane

4.11.5 Doped and dedoped polyaniline / PVDF membranes

In accordance with the procedure described in III-3.2.5, the membranes were doped with gaseous hydrochloric acid and dedoped with ammonia gas.

Figure III-25: Polyaniline / PVDF doped with HCl and dedoped with NH₄Cl. Ammonium chloride crystals can be seen on the surface of the membrane
Figures III-25 and III-26 show the edge of a membrane after the dedoping procedure. The membrane consists of the PVDF support and the polyaniline layer. On top of the polyaniline layer, ammonium chloride crystals can be seen. Interestingly, the ammonium chloride is not uniform on the surface, but randomly distributed.

Figure III-26: PAni / PVDF composite membrane doped with HCl and dedoped with NH₄Cl. Ammonium chloride crystals on the surface and inside the support material

The formation of crystals may not only be restricted to the surface of the membranes. Figure III-26 shows an area of the membrane where ammonium chloride crystallisation occurred via a small hole (microporous defect) inside the support structure.

In summary, doping processes cause changes in the polymer matrix that are beyond the resolution of SEM.

SEM examination demonstrates that it is possible to combine porous support materials with polyaniline. The polyaniline / PVDF composite membrane is of special interest: while in the other composite materials the polyaniline layer is either "fused" with the support (in the case of ethylcellulose or ethylacetate), other materials (polyetherimide) tend to decompose.

Polyaniline membranes combine well with PVDF supports. The polyaniline layer can still be separated mechanically from the support in order to measure the thickness.

Surface treatment with POS seals the polyaniline. A POS thickness of less than 0.3μm means a negligible resistance to permeating gases. In this work, the combination of polymeric support materials with polyaniline and POS has been demonstrated for the first time.
Literature Chapter III

Literature Part III


15. V. Sauerland and R. N. Schindler, "A mass spectrometric investigation of polyaniline using photoionization" publication, Institut für Physikalische Chemie Universität Kiel, Germany


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5 Sorption on polyaniline

For permeation studies sorption experiments give precious information on sorption modes. As discussed in Part I, the knowledge of the sorption mode (and thereby the related coefficients) finally allows to assess potential transport modes.

In the following, sorption experiments were carried out using a micro-force balance in the case of pressures from 0 to 1 bar, and a sorption cell for pressures from 1 to 73 bar. The test samples consisted of dedoped and HCl-doped polyaniline powders.

5.1 Micro-force balance

Figures IV-1 to IV-3 show the sorbed gas volume \( S \) in \( \text{cm}^3_{\text{STP}} / \text{cm}^3 \) polyaniline as a function of the applied pressure. The tests were carried out with the gases \( \text{N}_2, \text{O}_2 \) and \( \text{CO}_2 \).

In the case of \( \text{N}_2 \) and \( \text{O}_2 \) (Figures IV-1 and IV-2) the isotherms consist of the mean values of three single sorption tests for each data point, and the \( \text{CO}_2 \) sorption isotherms (cf. Figure IV-3) represent the mean value of eight test runs.

Sorption is in the order \( S_{\text{CO}_2} > S_{\text{O}_2} > S_{\text{N}_2} \). A higher affinity to polyaniline salt (compared to the base form) is indicated by higher sorption on this exchange state. The amount of sorbed gas for the doped sample is almost twice that of polyaniline base. The sorption isotherms of \( \text{N}_2 \) and \( \text{O}_2 \) in this pressure range are obviously analogous to the Henry sorption mode.
Determination of gas transport properties

Oxygen possibly, and much more significantly CO₂, produce isotherms which typically indicate sorption according to the Dual-mode model. Due to the small pressure ranges that were covered by this test method, additional examinations were performed:

Figure IV-2: Microbalance: sorption of O₂ on PANi-ES (HCl) and PANi-EB powder

Figure IV-3: Microbalance: sorption of CO₂ on PANi-ES (HCl) and PANi-EB powder
Sorption tests at higher pressures as presented in Chapter IV-5.2 give a more detailed view of the shape of the sorption isotherms and the underlying sorption mode.

5.2 Pressure decay method

The following sorption experiments were performed at pressures up to 73 bar, by using the pressure decay method. In Figures IV-4 and IV-5 sorption is presented as a function of the gas pressure applied. The experimental data are compared to the data calculated in accordance with the Dual-mode model, Langmuir sorption isotherms, and/or the BET sorption model. The parameters of the different sorption models are listed in Tables IV-1 to IV-3.

Regardless of the pressure applied, the amount of sorbed gas $S$ is in the order $S_{CO_2} > S_{O_2} > S_{N_2}$.

In agreement with the experimental sorption data that were obtained using the microbalance (in Chapter IV-5.1), the gases have a higher affinity to the doped state of polyaniline, and additionally sorption on polyaniline salt always exceeds sorption on the base form.

In the case of doped polyaniline, sorption of oxygen (Figure IV-4) is likely to occur in accordance with the Dual-mode mechanism. This is indicated by the market increase of the sorption vs. pressure graph at the beginning which continues with a linear part. In contrast to sorption of nitrogen (Figure IV-5), the pressure dependence of oxygen sorption is noticeably higher, especially at low pressures. The emeraldine base has a significantly weaker affinity to the gas than the doped state.

![Figure IV-4: Sorption cell: Experimental results and Dual-mode results for O₂ sorption on PANi-ES (HCl) and PANi-EB powder](image-url)
Determination of gas transport properties

Figure IV-5: Sorption cell: Experimental results and Dual-mode results for N₂ sorption on PANi-ES (HCl) and PANi-EB powder

At higher pressures oxygen sorption on the base is only about half of that on doped polyaniline, whereas at lower pressures the difference is less significant.

These isotherms are typical of sorption according to the Dual-mode model:
- a steep increase at the beginning (0 to about 4 bar) indicates the dominance of Langmuir sorption, and the linear increase (4-15 bar) reflects sorption in accordance with Henry dissolution. Also the sorption isotherm of polyaniline base follows this trend. It can be seen that the experimental curves correspond quite well with the data according to the Dual-mode theory.

Figure IV-5 presents sorption of nitrogen. These isotherms appear to be linear at the beginning (0-10 bar) and there seems to exhibit Henry-type sorption.

The overall shape of the isotherms cover a wide pressure range, and they make sorption according to Langmuir obvious. Langmuir-type sorption has a type I isotherm (see Chapter I-2.3.1) which is characterized by a defined saturation limit.

Saturation behaviour indicates that adsorption of nitrogen occurs at preferential sites such as microvoids and pores within the polyaniline powders. Only when those sites are almost completely occupied, an additional small amount of gas dissolves randomly dispersed within the polymer and finally the isotherm shows saturation behaviour.
The coefficients of the Dual-mode model were determined graphically as described in Chapter I-2.3.2. The first data point that belongs to the linear part of the isotherm is at 40 bar. By means of equations I-44 to I-48 the respective coefficients were calculated successively, starting with the determination of the solubility coefficient $S$.

It can be derived from the experimental data that in this pressure region saturation effects are still present. For this reason, especially at higher pressures, the data used calculate sorption to be below the experimental findings, whereas the conformity at low pressures is quite good. The experimental data correlates much better with the data according to the Langmuir model: almost complete agreement with the experimental data can be seen. This means that with respect to the mechanism of nitrogen transport, Henry-solubility only plays a minor role.

The isotherms for carbon dioxide differ quite significantly from those of the other gases (cf. Figures IV-6 and IV-7): The experimentally obtained isotherms are of sigmoid shape and have a saddle point. While Langmuir sorption prevails at the beginning, a Henry-like sorption behaviour (indicated by linearity) is dominant over a wide pressure range, beginning at 5bar up to approximately 35-40bar.

As discussed for oxygen, the sorption isotherm starts with the typical non-linear Langmuir sorption at the beginning. This section ends at 5bar (cf. also Figure I-7).

With increasing pressure the sorption isotherm increases strongly. The curve shows a saddle point at about 20bar, typical also for type II sorption (cf. Figure also I-9). This may indicate the filling of microvoids, capillary-condensation and multilayer-adsorption. Unlike in the case of the permanent gases oxygen and nitrogen, (multilayer) condensation of carbon dioxide on the polymer (and with this an increasing amount of "condensed gas") at comparatively high pressures and close to the critical temperature $T_c$ may explain the strong increase of sorption above 40bar.

The parameters for the Dual-mode model were obtained by two means: the Dual-mode curve on the left side (Dual-mode at low pressures) shows the calculated permeability according to the data from the micro balance sorption experiments (cf. Figure IV-1 and Table IV-3). Most likely the pressure range of this method was too small to get reliable results up to 35bar. The Dual-mode coefficients that were determined at a higher pressure come quite close to the experimental data. Still higher pressures lead to an almost exponential increase of the curve, whereas the Dual-mode plot still is linear.
Table IV-1: Dual-mode coefficients from gas sorption experiments on polyaniline base and polyaniline HCl salt, with \( (k_D \text{ and } b') \cdot 10^3 \)

<table>
<thead>
<tr>
<th>Gas</th>
<th>Exchange state</th>
<th>Coefficient</th>
<th>Coefficient</th>
<th>Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( k_D (\frac{\text{cm}^3\text{STP}}{\text{cm}^3\text{polymer} \cdot \text{cmHg}}) )</td>
<td>( C'_p (\frac{\text{cm}^3\text{STP}}{\text{cm}^3\text{polymer}}) )</td>
<td>( b' (\frac{1}{\text{cmHg}}) )</td>
</tr>
<tr>
<td>CO₂</td>
<td>EB</td>
<td>10,16</td>
<td>3,97</td>
<td>2,87</td>
</tr>
<tr>
<td></td>
<td>ES</td>
<td>13,49</td>
<td>13,01</td>
<td>4,46</td>
</tr>
<tr>
<td>CO₂</td>
<td>microbalance</td>
<td>59,17</td>
<td>3,26</td>
<td>147,71</td>
</tr>
<tr>
<td></td>
<td>ES</td>
<td>83,14</td>
<td>8,42</td>
<td>253,61</td>
</tr>
<tr>
<td>O₂</td>
<td>EB</td>
<td>9,49</td>
<td>2,29</td>
<td>40,08</td>
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<tr>
<td></td>
<td>ES</td>
<td>13,75</td>
<td>1,05</td>
<td>4,70</td>
</tr>
<tr>
<td>N₂</td>
<td>EB</td>
<td>1,24</td>
<td>12,31</td>
<td>0,70</td>
</tr>
<tr>
<td></td>
<td>ES</td>
<td>2,42</td>
<td>12,19</td>
<td>0,82</td>
</tr>
</tbody>
</table>

Table IV-2: Langmuir coefficients, calculated from gas sorption experiments on polyaniline base and polyaniline HCl salt

<table>
<thead>
<tr>
<th>Gas</th>
<th>Exchange state</th>
<th>Coefficient</th>
<th>Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( C'_p (\frac{\text{cm}^3\text{STP}}{\text{cm}^3\text{polymer}}) )</td>
<td>( b' (\frac{1}{\text{cmHg}}) )</td>
</tr>
<tr>
<td>N₂</td>
<td>EB</td>
<td>31,95</td>
<td>0,0221</td>
</tr>
<tr>
<td></td>
<td>ES</td>
<td>42,74</td>
<td>0,0203</td>
</tr>
</tbody>
</table>

Table IV-3: BET coefficients, determined from the graphic solution of \( \frac{p_r}{[(1 - p_r) \cdot V]} \) vs. \( p_r \) plot, where \( p_r = \frac{p^*}{p_0} \)

<table>
<thead>
<tr>
<th>Exchange state</th>
<th>( p (\text{CO}_2 \text{ at } 298K) ) †</th>
<th>c</th>
<th>( V_{\text{mon}} / \text{cm}^3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>EB</td>
<td>64,097bar</td>
<td>66,4</td>
<td>15,57</td>
</tr>
<tr>
<td>ES</td>
<td>64,097bar</td>
<td>362,1</td>
<td>26,14</td>
</tr>
</tbody>
</table>

† Numerical Database for Chemical Engineering, "Dortmunder Datenbank", (DDB)

The BET model gives the best fit to the experimental data and covers the whole pressure range. It predicts a saturation point in the middle of the graph (cf. Figure I-9), as well as the shape of the curve at the beginning which is due to the filling of preferential sites within the adsorbate and also the almost exponential increase at the end of the pressure range investigated, which refers to multi-layer adsorption. CO₂ sorption on polyaniline salt and base differs in the amount of adsorbed gas, whereas the sorption mode is similar. It is interesting to note that at low pres-
Determination of gas transport properties

...sure the Dual-mode model describes the experimental data better. At more than 10bar, the BET model fits the experimental data better.

The Dual-mode coefficients and the BET-related coefficients are listed in Tables 1-IV and 3-IV, while Table IV-2 shows the Langmuir coefficients.

![Figure IV-6: Comparison of experimental CO₂ sorption isotherm with BET-model and Langmuir sorption isotherm. Sample: PAni-EB powder](image)

![Figure IV-7: Comparison of experimental CO₂ sorption isotherm with BET-model and Dual-mode isotherm. Sample: PAni-ES (HCl) powder](image)
6 Determination of gas transport properties

In the following sections, the results of examination of gas transport properties of various polyaniline membranes will be presented and discussed. Also, an outline of results obtained by selected means of various testing devices will be given. This includes a wide range of possible parameters that exert influence on permeation properties such as temperature, pressure, doping, material thickness, or coating, to name a few.

6.1 As-cast polyaniline membranes with microporous defects

Microscopic defects in the membrane result in comparatively high permeation rates (see Chapter II-2.1) in combination with separation factors far below those observed for dense membranes. Figure IV-8 shows a $p$ vs. $t$ plot in the downstream part of the diffusion cell during permeation experiments with microporous polyaniline membranes.

![Permeation of various gases through microporous as-cast polyaniline membrane](image)

Figure IV-8: Permeation of various gases through microporous as-cast polyaniline membrane, $A_M = 3.2\,\text{cm}^2$, $t_M = 15.5\,\mu\text{m}$, $p = 1\,\text{bar}$

From these data, ideal separation factors for all gas pairs were calculated. Only a few microporous defects result in Knudsen diffusion as the dominant transport mechanism. If solution-diffusion is the dominant transport mechanism, the actual selectivity is significantly different from microporous membranes as shown in Table IV-4. Approximately one in four polyaniline membranes prepared showed unexpectedly high permeation rates. These high permeation rates derived from regularly distributed pores and not
Determination of gas transport properties from randomly occurring microporous defects (cf. Figure III-16). Electron micrographs of the cross-sections of prepared polyaniline membranes show small holes of approximately 0.4\( \mu \)m diameter, whereas others appear to be free of defects.

Table IV-4: Ideal separation factors for microporous polyaniline membranes

<table>
<thead>
<tr>
<th>Gas pair</th>
<th>Ideal separation factor</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experimental results ( \alpha = (P_1 / P_2) )</td>
<td>Knudsen Diffusion ( \alpha = (M_{w2} / M_{w1})^{0.5} )</td>
</tr>
<tr>
<td>( \text{N}_2/\text{O}_2 )</td>
<td>1.07</td>
<td>1.07</td>
</tr>
<tr>
<td>( \text{O}_2/\text{CO}_2 )</td>
<td>1.32</td>
<td>1.17</td>
</tr>
<tr>
<td>( \text{N}_2/\text{CO}_2 )</td>
<td>1.41</td>
<td>1.25</td>
</tr>
<tr>
<td>( \text{H}_2/\text{N}_2 )</td>
<td>3.54</td>
<td>3.74</td>
</tr>
<tr>
<td>( \text{H}_2/\text{CO}_2 )</td>
<td>4.52</td>
<td>4.69</td>
</tr>
<tr>
<td>( \text{H}_2/\text{O}_2 )</td>
<td>3.65</td>
<td>4.00</td>
</tr>
</tbody>
</table>

Microporosity can easily be proven by measuring ideal separation factors for various gas pairs and comparing them to those predicted for Knudsen diffusion. It is apparent from Table IV-4 that the ideal separation factors derived from the permeabilities of various gases through microporous polyaniline membranes are very similar to the predicted ideal separation factor in the Knudsen regime.
6.2 Permeation through defect-free polyaniline membranes

Dense membranes can easily be recognized if the permeation rates of e.g. hydrogen and nitrogen are compared. A typical separation factor for a dense membrane ($\alpha_{\text{H}_2/\text{N}_2} > 50$) is far above the Knudsen separation factor ($\alpha_{\text{H}_2/\text{N}_2} \sim 4$) for this gas pair. Figure IV-9 shows a typical permeation plot for such an essentially pore-free membrane.

![Figure IV-9: Typical permeation plot of defect-free polyaniline membrane, $A_M = 7.5\text{cm}^2$, $t_M = 10\mu$m, $P_{\text{Feed}} = 2.5\text{bar}$](image)

If Figure IV-9 is compared to the microporous membrane, it is apparent that the permeation rates of the individual gases differ significantly so that the dominant transport mechanism may be assumed to be solution-diffusion controlled.

In the following sections the permeation rates of the gases H$_2$, O$_2$, N$_2$ and CO$_2$ through various types of membranes are evaluated.

6.3 Unsupported polyaniline membranes

Unsupported polyaniline membranes were tested in order to assess the permeation-related properties of these films. Although data from some literature data is available for unsupported
Determination of gas transport properties

membranes, it seemed important to compare the membrane materials we produced with those data of the literature.

Additionally, basic knowledge of material properties was to be increased as this will be most useful for further studies.

6.3.1 Permeation characteristics of different membrane exchange states

Permeation tests were carried out with membranes in different oxidation states, in the following denoted as: "as-cast" (as prepared; undoped exchange state), "doped", "dedoped" and "redoped" (compare experimental section II-3.2.5). The membranes were unsupported and had a thickness of 10 to 15µm. Figure IV-10 shows the permeability of the gases H₂, O₂, N₂, and CO₂ for the different exchange states of polyaniline.

![Figure IV-10: Permeability (Barrer) of unsupported polyaniline membranes, \( A_M = 9.6 \text{cm}^2 \), \( t_M = 10-15\mu \text{m} \), \( p_{\text{Feed}} = 1-2.7 \text{bar} \)]

The permeability decreases in the order \( H_2 > CO_2 > O_2 > N_2 \), regardless of the exchange state of the membrane.

The degree of gas permeability (decrease) of the different membrane states is dedoped > as-cast > redoped > doped. Due to the small permeability of \( O_2 \), \( N_2 \) and \( CO_2 \) across the completely doped membrane (below 0.002 Barrer), only the permeability of hydrogen could be determined. It was found to be 0.55 Barrer.
Determination of gas transport properties

Dedoping of the membranes resulted in the creation of the most permeable membrane modification. At the same time a decrease in selectivity for the gas pairs containing nitrogen was observed whereas the selectivity for the other gas pairs increased.

It is noteworthy that the permeability of nitrogen across the as-cast membrane is rather high compared to that found by other researchers (cf. Tables IV-5 and 6).

Table IV-5 presents permeation data in as gas flux and Barrer. The corresponding selectivities are listed in Table IV-7.

Concerning the as-cast membrane, it is noteworthy that in the case of gas pairs containing nitrogen separation factors were found that are comparatively high compared to those of other researchers.

Table IV-5: Gas flux $J \left(10^{-4} \text{ Nm}^3/\text{h bar m}^2\right)$ and permeability (Barrer, bracketed) for unsupported polyaniline membranes, this work

<table>
<thead>
<tr>
<th>Exchange State</th>
<th>Gas</th>
<th>H$_2$</th>
<th>CO$_2$</th>
<th>O$_2$</th>
<th>N$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-cast</td>
<td></td>
<td>3.969 (1.447)</td>
<td>0.65 (0.258)</td>
<td>0.21 (0.083)</td>
<td>0.0213 (0.008)</td>
</tr>
<tr>
<td>Doped</td>
<td></td>
<td>0.866 (0.546)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dedoped</td>
<td></td>
<td>8.586 (3.807)</td>
<td>1.211 (0.566)</td>
<td>0.2242 (0.1052)</td>
<td>0.111 (0.052)</td>
</tr>
<tr>
<td>Redoped</td>
<td></td>
<td>1.02 (0.7)</td>
<td>0.112 (0.076)</td>
<td>0.0325 (0.022)</td>
<td>0.0068 (0.005)</td>
</tr>
</tbody>
</table>

Table IV-6: Permeability (Barrer) of various polyaniline membranes. Permeation data obtained by other researchers

<table>
<thead>
<tr>
<th>Exchange State</th>
<th>Gas</th>
<th>H$_2$</th>
<th>CO$_2$</th>
<th>O$_2$</th>
<th>N$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-cast</td>
<td></td>
<td>2.46 - 3.707</td>
<td>0.476 - 0.67</td>
<td>0.1 - 0.121</td>
<td>0.017 - 0.019</td>
</tr>
<tr>
<td>Doped</td>
<td></td>
<td>0.121 - 1.4</td>
<td>&lt; 0.002 - 0.035</td>
<td>&lt; 0.002 - 0.016</td>
<td>&lt; 0.002 - 0.016</td>
</tr>
<tr>
<td>Dedoped</td>
<td></td>
<td>3.14 - 6.05</td>
<td>0.568 - 0.985</td>
<td>0.135 - 0.195</td>
<td>0.01 - 0.021</td>
</tr>
<tr>
<td>Redoped</td>
<td></td>
<td>1.41 - 4.35</td>
<td>0.156 - 0.547</td>
<td>0.07 - 0.142</td>
<td>0.0001 - 0.01</td>
</tr>
</tbody>
</table>

Table IV-7: Ideal separation factors for unsupported polyaniline membranes (calculated from Table IV-5)

<table>
<thead>
<tr>
<th>Exchange state</th>
<th>Gas pair</th>
<th>H$_2$/CO$_2$</th>
<th>H$_2$/O$_2$</th>
<th>H$_2$/N$_2$</th>
<th>CO$_2$/O$_2$</th>
<th>CO$_2$/N$_2$</th>
<th>O$_2$/N$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-cast</td>
<td></td>
<td>6</td>
<td>17</td>
<td>180</td>
<td>3</td>
<td>32</td>
<td>10</td>
</tr>
<tr>
<td>Undoped</td>
<td></td>
<td>7</td>
<td>36</td>
<td>73</td>
<td>5</td>
<td>11</td>
<td>2</td>
</tr>
<tr>
<td>Redoped</td>
<td></td>
<td>9</td>
<td>32</td>
<td>152</td>
<td>3.5</td>
<td>17</td>
<td>5</td>
</tr>
</tbody>
</table>
Redoping of the membrane results in an increase of selectivity compared to the dedoped modification, whereas the selectivity of the gas pair CO₂/O₂ and H₂/O₂ decreases. Results of further examination of the redoped exchange state will be presented in section IV-6.4.2. Gas pairs containing nitrogen are of special concern with regard to membrane selectivity. Due to the comparatively low permeability of nitrogen, smallest changes of the experimental setup can influence the results.

The precision of the ideal separation factor α, the quotient of permeabilities of the two gases involved, will decrease significantly if the permeability of the gases is at the limit of the detecting range of the permeation apparatus (cf. Error Discussion).

During the course of this work, it was found that the time to reach steady-state permeation for nitrogen was in about 8 hours, even for very thin membranes.

For the examinations in the following chapters, the results that were discussed in this section give an idea of the magnitudes of the permeation rate and the separation factors involved.

For large scale separation processes, it will be necessary to achieve:

- reproducible membrane properties
- an increase of stability
- large membrane areas
- and a decrease of film thickness for an increase of flux

### 6.4 Permeability and separation factor as functions of membrane thickness

The literature available only reports on permeation results for single polyaniline membranes. There is little evidence for the reproducibility of that data. Also very little has also been published on the effects of production parameters such as the underlying polymerisation process, curing times, curing temperature, substrate used, and storage times of the film in water, to name just a few.

#### 6.4.1 Unsupported dedoped membranes

The permeabilities of H₂ and CO₂ through dense dedoped polyaniline membranes are shown in Figure IV-11 as a function of membrane thickness. The resulting ideal separation factor is also shown. The H₂/CO₂ separation factor essentially remains constant with increasing membrane thickness. However, the permeabilities of H₂ and CO₂ change from membrane to membrane.
Determination of gas transport properties

The data do not suggest any increase of the ideal separation factor with increasing film thickness. The average ideal separation factor found for the gas pair H₂/CO₂ was 5.23 with a standard deviation of 0.19. This compares well with ideal separation factors and permeabilities reported by Anderson¹, Kaner et al.²,³, Rebattet et al.⁴, and Chang et al.⁵, who found ideal separation factors in the range between 4 and 9 (cf. Table IV-8).

It is interesting to note that Kuwabata et al.⁶ report about increasing separation factors together with an increase membrane thickness. They also found a maximum for the ideal separation factor for the gas pair O₂/N₂ at a film thickness of more than 20µm. They consider their membranes to be defect-free.

Table IV-8: Permeabilities and ideal separation factors for dedoped polyaniline membranes found by different researchers

<table>
<thead>
<tr>
<th>Researcher</th>
<th>Ideal separation factor</th>
<th>Permeability / Barrer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>α</td>
<td>P H₂</td>
</tr>
<tr>
<td>Anderson¹</td>
<td>6.1</td>
<td>6.05</td>
</tr>
<tr>
<td>Kaner et al.³</td>
<td>6.8</td>
<td>17.6</td>
</tr>
<tr>
<td>Kaner et al.²</td>
<td>8.9</td>
<td>11.6</td>
</tr>
<tr>
<td>Rebattet et al.⁴</td>
<td>8</td>
<td>4.53</td>
</tr>
<tr>
<td>Chang et al.⁵</td>
<td>4.07</td>
<td>3.14</td>
</tr>
<tr>
<td>Own results</td>
<td>5.23</td>
<td>3.33</td>
</tr>
</tbody>
</table>

Hydrogen and carbon dioxide were chosen in this work because even for the thickest membranes the permeability of the gases lies far above the detection limit.
Determination of gas transport properties

Figure IV-11: Permeation and ideal separation factor of H₂ and CO₂ through dedoped polyaniline membranes with different thicknesses, $A_M = 7.1 - 9.6 \text{cm}^2$, $p_{Feed} = 1 \text{bar}$

6.4.2 Redoped polyaniline membranes

Redoped membranes are of special interest as this exchange state has been shown to exhibit the highest selectivities of all exchange states of polyaniline\textsuperscript{1,4,7}.

In order to determine the influence of varying thickness on permeability and ideal separation factor, seven tests with membranes of different thickness were conducted with different gases. The permeation tests were carried out with an upstream pressure of 2.7 bar to facilitate the measurement of O₂ and N₂ permeabilities. Due to the reduced flux through redoped membranes, film thicknesses between 9 and 29µm were examined.

It is apparent from Figure IV-12 that the membrane thickness has no effect on the permeability of the redoped membranes with respect to H₂, CO₂, O₂ and N₂. The resulting ideal separation factors as functions of membrane thickness are given in Table IV-9. It is reasonable to assume that very thin, defect-free polyaniline layers should show similar separation properties as more conventional thicker layers (10 µm or more).

The average ideal separation factors for all gas pairs considered, as well as the resulting standard deviations are given in Table IV-11.
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In particular, the ideal separation factors for the gas pairs \( \text{H}_2/\text{N}_2 \), \( \text{CO}_2/\text{N}_2 \) and \( \text{O}_2/\text{N}_2 \) were found to be somewhat smaller than those reported by Rebattet et al.\(^4\) (cf. Table IV-8). In general, the redoped membranes did not exhibit the extremely high separation factors reported by Anderson\(^1\) and Kaner et al.\(^2\) (cf. Table IV-12).

Table IV-9: Ideal separation factors for various gas pairs for redoped polyaniline membranes with different thicknesses; \( A_M = 9.6 \text{cm}^2 \), \( P_{\text{feed}} = 2.7 \text{bar} \)

<table>
<thead>
<tr>
<th>Thickness/µm</th>
<th>( \text{H}_2/\text{CO}_2 )</th>
<th>( \text{H}_2/\text{O}_2 )</th>
<th>( \text{H}_2/\text{N}_2 )</th>
<th>( \text{CO}_2/\text{O}_2 )</th>
<th>( \text{CO}_2/\text{N}_2 )</th>
<th>( \text{O}_2/\text{N}_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.2</td>
<td>7.0</td>
<td>28.3</td>
<td>120.9</td>
<td>4.1</td>
<td>17.4</td>
<td>4.3</td>
</tr>
<tr>
<td>14.4</td>
<td>10.0</td>
<td>30.1</td>
<td>157.8</td>
<td>3.0</td>
<td>15.8</td>
<td>5.2</td>
</tr>
<tr>
<td>16</td>
<td>9.1</td>
<td>26.3</td>
<td>154.9</td>
<td>2.9</td>
<td>17.0</td>
<td>5.9</td>
</tr>
<tr>
<td>17.4</td>
<td>9.5</td>
<td>32.3</td>
<td>162.0</td>
<td>3.4</td>
<td>17.1</td>
<td>5.0</td>
</tr>
<tr>
<td>19.7</td>
<td>10.0</td>
<td>38.1</td>
<td>200.1</td>
<td>3.8</td>
<td>20.0</td>
<td>5.2</td>
</tr>
<tr>
<td>20.8</td>
<td>7.6</td>
<td>29.5</td>
<td>133.9</td>
<td>3.9</td>
<td>17.7</td>
<td>4.5</td>
</tr>
<tr>
<td>28.4</td>
<td>10.0</td>
<td>33.1</td>
<td>125.9</td>
<td>3.3</td>
<td>12.6</td>
<td>3.8</td>
</tr>
</tbody>
</table>

It should be noted that the extraordinarily high separation factors which were calculated using Anderson’s results had been observed for gas pairs containing slowly permeating gases, e.g. \( 10^{-4} \) Barrer for nitrogen. With a permeability for oxygen (0.07 Barrer) through the redoped mem-
Determination of gas transport properties

brane the separation factor calculated for the gas pair N₂/O₂ consequently would be 700; This lay orders of magnitude above the values that have ever been published for this gas pair (cf. also Table IV-10 to IV-12).

Anderson mentions difficulties with measuring permeability of nitrogen due to its extremely low flux. One may argue that Anderson’s results are somewhat contradictory since on the one hand he claims that for the doped membranes 0.002 Barrer is beyond his detection limit¹, and on the other hand he reports to have measured 0.0001 Barrer for his redoped membranes. There are also significant differences between the results published by Anderson¹ and Kaner et al.⁸: if we calculate the ideal separation factors for the gas pair CO₂/CH₄ from the permeabilities of the individual gases (e.g. α = 336, as published, vs. α = 1580, as calculated), there appears to be a very big difference, probably resulting from a lack of precision when measuring the small permeability of CH₄ (or N₂) through these membranes. Extremely high separation factors for the redoped membranes result from that. Similarly, the ideal separation factors stated by Rebattet et al.⁴ are higher for those gas pairs that contain nitrogen (cf. Table IV-12). A similar argument applies in this case.

Unfortunately, researchers do not mention how many membranes were tested in each run, and they do not explain how the thickness of their membranes was determined. Both points are also very important for permeation calculations and the evaluation of ideal separation factors.

Table IV-10: Published permeation data for polyaniline membranes, and own results

<table>
<thead>
<tr>
<th>Researcher</th>
<th>Permeability of various gases through redoped polyaniline membranes, P / Barrer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂</td>
</tr>
<tr>
<td>Anderson¹</td>
<td>1.41</td>
</tr>
<tr>
<td>Kaner et al.²</td>
<td>7.18</td>
</tr>
<tr>
<td>Rebattet et al.⁴</td>
<td>4.35</td>
</tr>
<tr>
<td>Own results (free-stand., tₘ 9-29µm)</td>
<td>0.69</td>
</tr>
</tbody>
</table>

Table IV-11: Mean values and standard deviation of ideal separation factors for various gas pairs; redoped polyaniline membranes

<table>
<thead>
<tr>
<th>α = P₁ / P₂</th>
<th>Gas pair</th>
<th>H₂/CO₂</th>
<th>H₂/O₂</th>
<th>H₂/N₂</th>
<th>CO₂/O₂</th>
<th>CO₂/N₂</th>
<th>O₂/N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average of 28 membranes</td>
<td></td>
<td>9.02</td>
<td>31.12</td>
<td>150.78</td>
<td>3.49</td>
<td>16.78</td>
<td>4.86</td>
</tr>
<tr>
<td>Standard deviation</td>
<td></td>
<td>0.13</td>
<td>0.12</td>
<td>0.17</td>
<td>0.12</td>
<td>0.12</td>
<td>0.13</td>
</tr>
</tbody>
</table>
Determination of gas transport properties

Various polymeric materials such as polyvinylchloride, polyamide, polyester, polypropylene and others mostly have an isotropic morphology so that the permeability does not depend on film thickness\(^9\). In the case of polyaniline, anisotropic irregularities within the membrane should result in a non-linear shape of the \( p \) vs. \( t \) curve at steady state. Such effects can be caused by permeant-induced plastification, clustering, or the formation of transport channels\(^10\).

Table IV-12: Ideal separation factors for redoped polyaniline membranes calculated from the results of different researchers

<table>
<thead>
<tr>
<th>Ideal Separation factor ( \alpha ) of redoped membranes</th>
<th>Gas pair</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Investigator</td>
<td>( \text{H}_2/\text{CO}_2 )</td>
<td>( \text{H}_2/\text{O}_2 )</td>
</tr>
<tr>
<td>Anderson(^1)</td>
<td>9</td>
<td>20</td>
</tr>
<tr>
<td>Kaner \textit{et al.}(^2,3,7)</td>
<td>120</td>
<td>144</td>
</tr>
<tr>
<td>Rebattet \textit{et al.}(^8)</td>
<td>8</td>
<td>31</td>
</tr>
<tr>
<td>\textbf{Own results}</td>
<td>9</td>
<td>31</td>
</tr>
</tbody>
</table>

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7 Polyaniline-based composite membranes

By means of the new production process (described in Chapter II-4.2) dense, ultrathin polyaniline layers were combined with poly(vinylidenfluoride). Additionally, those membranes can be coated with polyorganosiloxanes (POS), coatings that allow plugging of micropores. The following examinations show permeation performance and selectivity of the new composite material.

7.1 Effect of thickness on membrane performance

Figure IV-13 illustrates the gas flux through an as-cast composite membrane as a function of polyaniline thickness. The membranes that were tested had an overall thickness of 62 to 105μm with an effective thickness of the polyaniline layer between 1.6 and 10.5μm.

The overall thickness of the membrane is indicated in the middle of the graph (bracketed). The test gases were H₂, CO₂, O₂ and N₂, and feed pressures were in the range of 1-1.5bar.

Permeation tests on the spongeous support showed that the gas flux through this material is some orders of magnitude higher as compared to unsupported polyaniline membranes and for this reason this material is not the determining factor for gas permeability in a composite membrane. As Figure IV-13 shows, the transport rate for all gases increased with decreasing membrane thickness.

Furthermore, the graph clearly indicates that even for the thinnest membrane the intrinsic gas separation properties of polyaniline were present.

This examination also supports the observation made that the transport rate J is nearly independent of the over all film thickness and therefore only depends on the thickness of the polyaniline layer.
Figure IV-13: Permeability of as-cast PAni / PVDF membranes related to the overall thickness and the thickness of the polyaniline-layer
7.2 Permeation through polyaniline / PVDF / POS membranes

In this section the performance of POS-coated membranes will be presented, with Figure IV-14 showing the permeability of H₂, CO₂, O₂, N₂ and CH₄ through a coated polyaniline / PVDF membrane, and Figure IV-15 presenting the respective separation factors. By coating with siloxanes undesired pinholes can be plugged in an effective way.

![Permeability of gases through a PAni / PVDF / POS membrane](image)

Figure IV-14: Permeability of a PAni / PVDF / POS membrane for various gases; \( A_M = 7.1 \text{cm}^2 \), \( P_{\text{feed}} = 1.2 - 1.5 \text{bar} \)

Beginning with the most permeable gas hydrogen the permeability of the gases is, in the order

\[
\text{H}_2 > \text{CO}_2 > \text{O}_2 > \text{N}_2 > \text{CH}_4.
\]

From the permeability and the separation factors it can be derived that no porosity existed in the membrane. The highest separation factor found is 136 for the gas pair H₂/CH₄, it is 40 for CO₂/CH₄ and 7 in the case of the gas pair O₂/N₂.

The investigations proved, that POS coating is an appropriate treatment for polyaniline surfaces if porosity is to be eliminated. It is noteworthy that the overall permeability of the membrane will not be affected by the POS layer. The reason is the high permeability of POS for gases. In composite membranes, the layer with the highest resistance to the permeating gas will determine the overall permeability of the membrane. For example: the permeation rate of CO₂ in the case of various siloxanes is 670-2900 Barrer⁰¹¹, whereas the permeability of the same gas through polyaniline is only 0.26-0.56 Barrer (cf. Table IV-6).

Another desirable effect of coating is the fact that the siloxane layer protects the polyaniline surface from environmental influences such as unintended doping by compounds in the feed.
Composite membranes based on polyaniline

This observation was made during doping tests with polyaniline films: pieces of coated and uncoated polyaniline film were immersed into 1M HCl. While the copper like color of the uncoated film rapidly changed to a greenish blue, the coated material kept its colour for hours.

![Graph showing ideal separation factors for various gas pairs](image)

Figure IV-15: Ideal separation factor of PAni / PVDF / POS membrane for various gases

Figure IV-15 shows the ideal separation factors $\alpha$ that were calculated from the permeabilities of the individual gases. Table IV-13 directly compares $\alpha$ of an unsupported membrane with that of a coated composite membrane. The results reveal that the selectivity of those coated composite membranes remains comparable to that of uncoated ones. Some deviations can be seen for the gas pairs containing nitrogen. The same arguments as stated in Chapter IV-6.4 may apply here: in the case of unsupported membranes, the permeation tests might have been stopped at a time when permeability had not already reached steady-state conditions. For this reason, $\alpha$ appears to be comparatively high for slowly permeating gases such as nitrogen.

<table>
<thead>
<tr>
<th>Exchange State</th>
<th>H$_2$/CO$_2$</th>
<th>H$_2$/O$_2$</th>
<th>H$_2$/N$_2$</th>
<th>CO$_2$/O$_2$</th>
<th>CO$_2$/N$_2$</th>
<th>O$_2$/N$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-cast, unsupported</td>
<td>6</td>
<td>17</td>
<td>180</td>
<td>3</td>
<td>32</td>
<td>10</td>
</tr>
<tr>
<td>As-cast, composite</td>
<td>3.5</td>
<td>15</td>
<td>102</td>
<td>4.5</td>
<td>30</td>
<td>7</td>
</tr>
</tbody>
</table>

Table IV-13: Comparison of ideal separation factors for various gas pairs, calculated for unsupported and supported polyaniline membranes
7.2.1 Defects in polyaniline / PVDF / POS composite membranes

Plugging of pinhole defects does not always work. Figure IV-16 shows a set of permeation plots in which pores became "unplugged" during the permeation test.

![Figure IV-16: Permeation of various gases through a doped PAni / PVDF / POS membrane with microporous defects; $A_M = 7.1 \text{ cm}^2$](image)

The reason for unexpectedly occurring defects in this case is insufficient drying time, which means that the POS did not polymerise completely. As a result, microscopic holes are plugged with partially polymerised siloxane of low viscosity. If pressure is applied, the siloxane will just be squeezed out of the pores. Figure IV-16 illustrates such a process. The permeation plot of nitrogen shows this effect three times: every time a pore is pressed open it can be seen by an instant change in slope. This is quite impressive, as it shows the enormous effect of just one micropore on the permeation rate.

7.3 Validation tests with constant volume / variable pressure method

Permeation tests using the constant volume / variable pressure (CVVP) method were made in order to compare the results of each of the methods used before. The fully automated test device insured high reliability. These tests were carried out at the GKSS Forschungszentrum / Geesthacht GmbH, Germany.
Figure IV-17 shows permeability as a function of pressure. The permeabilities of the gases H₂, CO₂, O₂ and N₂ were tested at least 6 times. In the case of nitrogen, six permeation tests were made three times. The test sample was an as-cast polyaniline / PVDF composite membrane coated with POS.

In the case of nitrogen the feed pressure increased during the three repetitions: The first test started at 940 mbar, the second at about 942 mbar, and the third at 945 mbar. The increase of the feed pressure was due to temperature effects and inconsistencies of the pressure sensor. This effect is frequently observed for very slowly permeating gases when permeation tests last one hour or longer.

A possible change of the permeability caused by a change of feed pressure (e.g. 5 mbar) can be neglected. This is due to the fact that a change of 5 mbar is just about 0.5% of the total feed pressure. An impact on permeability can be considered to be outside the detection resolution.

The permeabilities of hydrogen, carbon dioxide and oxygen were determined to be within a narrow range.

An interesting phenomenon was observed in the case of nitrogen: the permeability of N₂ had a tendency to increase with increasing duration of the measurement, so that permeability had not reached steady state when the tests stopped. As it turned out, also repeated standard permeation tests yielded some p vs. t curves for nitrogen indicating an unexpectedly high time lag value.
Composite membranes based on polyaniline

The results that were obtained with constant volume tests also supports the findings obtained with the CVVP method: the permeation plots of nitrogen show a tendency to increase with increasing duration of the measurement. This indicates that the permeation rate had not reached steady state, yet.

It can be stated that the results obtained with the CVVP method and the pressure decay method compare well with each other.

If one compares Figure IV-18 with Figure IV-15 above, it becomes obvious that the ideal separation factors for the respective gas pairs are of the same magnitude.

![Ideal separation factors for gas pairs of an as-cast PANi / PVDF / POS membrane; calculated from permeabilities determined with CVVP method](image)

The separation factors in Figure IV-18 were calculated from the mean values of the validation tests. Compared to the coated composite material, composite membranes without POS coating (cf. Figure IV-24) have slightly higher separation factors.
Composite membranes based on polyaniline

7.5 Permeability and separation factors for coated ceramic membranes

Some selected porous support materials can be coated with polyaniline in order to overcome mechanical stability problems of thin polyaniline films. In the following, ceramic membranes (TAMI®, pore size (surface): 0.14µm) were coated with polyaniline and subsequently sealed with POS.

![Permeability of various gases through TAMI® ceramic coated with PAni / POS layer, p = 1-7bar, A_M = 7,1cm](image)

Figure IV-19: Permeability of various gases through TAMIR® ceramic coated with PAni / POS layer, p = 1-7bar, A_M = 7,1cm

Figure IV-19 shows that just as well as for the other polyaniline-based membranes, the permeation rates have the order H<sub>2</sub> > CO<sub>2</sub> > O<sub>2</sub> > N<sub>2</sub> > CH<sub>4</sub>. With some exceptions the permeabilities and the separation factors are in the same range as the results presented in the previous sections. The additionally tested gas methane was found to be the slowest permeating gas so that for gas pairs containing methane the separation factor is even higher than for gas pairs containing nitrogen (cf. Figure IV-20).

The permeation tests on coated ceramic materials give evidence of the usability of polyaniline-coated ceramic membranes for gas separation due to the fact that the intrinsic separation properties of polyaniline can be transferred to the ceramic membrane without problem. Ceramic support materials offer an interesting alternative to polymeric carriers since resistance against solvents and higher temperatures is ensured. Furthermore, gas separation can be carried out at
Composite membranes based on polyaniline

high pressures. This may be of interest when separating gas pairs which contain a gas that permeates even more slowly than nitrogen.

Also, this can make permeation tests possible in pressure regions for which diffusion processes have not been described yet.

Figure IV-20: Ideal separation factor of various gas pairs permeating through TAMIC® ceramic coated with PAni / POS layer

Besides application in the gas separation field, the combination of polyaniline with ceramic materials offers some prospects for the separation of liquid mixtures of solvents or separation by pervaporation, since both materials (PAni and ceramics) are stable enough for such separation applications. Nevertheless, for such potential kinds of applications, solvent-induced plasticisation effects must be considered.
8 Change of permeation rate by doping

In processes where a defined gas flux or a certain ratio of process and carrier gases or purge gases is required, switchable membranes would be of interest, e.g. in ammonia synthesis. "Switching" in this case means a change of the separation factor and the gas transmission rate. The question a rises as to what will the permeation rate will be in the case of sudden introduction of anions into the membrane and during removal of the dopants.

8.1 Doping and dedoping of polyaniline / PVDF composite membranes

Figures IV-21 and IV-22 show the permeation of hydrogen through polyaniline / PVDF composite membranes. In these tests, doping and dedoping of the membrane during the permeation process changed the gas flux immediately. The three membrane exchange states are shown as regions 1, 2 and 3, referring to the membrane states "as-cast", "doped" and "undoped". The corresponding linear trends are meant to emphasise to what extent the transport rate changes. The membranes were doped by introducing HCl from the gas phase (unlike the doping process in aqueous media) and dedoped by removing HCl with NH3. In order to introduce (remove) HCl into (from) the membrane, the permeating gas bubbled through a gas wash bottle filled with concentrated hydrochloric acid (or NH4OH, respectively), before reaching the membrane.

In Figures IV-21 and IV-22 the permeation rate of hydrogen is presented as a function of the membrane state, and additionally Tables IV-14 and IV-15 present the corresponding change of process parameters. The permeation rate for each membrane state is indicated in Nm³/ bar h m² and also mbar/s for reasons of comparison.

It can clearly be seen that the change of the doping state immediately changed the flux. In Figure IV-21, HCl is introduced into the gas feed after 200s and a sudden change of the permeability was observed.

The partial pressure of NH3, HCl and H2O(g) was low, compared to the partial pressure of hydrogen, so that effects caused by reduced partial pressure of hydrogen can be neglected as preceding tests showed: in order to assess the influence of water vapour, NH3 and HCl on the permeability of hydrogen, a gas wash bottle filled with the respective liquids was installed between the gas feed line and the permeation cell. In none of the cases (H2O(l), NH4OH(l), HCl(l)) this caused changes of more than 5% to the permeation rate.
These experiments present for the first time revealed the change of permeability of such polyaniline composite membranes in situ during the doping and dedoping process. The immediate change of permeability showed that doping and dedoping must be very fast reactions.

Figure IV-21: Permeating hydrogen through a PAni / PVDF membrane in the exchange states as-cast, doped, dedoped. Arrows indicate the change of the doping state of the membranes that occurred during the permeation process; $t_{\text{PAni-layer}} = 3\mu m$, $A_M = 7.1\, \text{cm}^2$.

The appearance of the membrane surface on the downstream side after the permeation tests was still copper-like. This indicates that this membrane side did not get doped.

The indication here is that under the chosen test conditions, doping of the membrane only takes place on the surface on the upstream side.

Tests for chloride (see Chapter II-3.2.5) on those doped membranes showed that the degree of doping was about 15-20%. This can be explained by the fact that the test only measured the average contents of chloride of the whole membrane; the existence of a doping gradient within the membrane, which is obviously present, can not be ascertained with this method.

XPS examination could be made to give a deeper insight into the penetration depth the dopant into the membranes.

Presumably, doping just the surface (instead of doping the whole membrane) might be sufficient to obtain the desired permeability and to regulate selectivity. This may be quite an interesting possibility due to the fact that brittleness increased dramatically when doping was carried out in aqueous media.
Change of permeation range by doping

Interestingly, the permeability in the dedoped state did not exceed the level of the as-cast state, as had been expected due to the results obtained in Chapter IV-6.3.1. The most likely reason for that is incomplete dedoping: after the NH₃ treatment, a slightly blue colour on the membrane surface indicated an incomplete exchange process. It is also important to note again that the downstream side remained undoped (copper colour).

Tests for chloride on those dedoped membranes (gently rinsed with distilled water) showed that the extent of doping was still 5-10%.

Furthermore, the membrane surface or the membrane matrix might be influenced by ammonium chloride crystals that were observed after the membrane treatments described. Micrographs (cf. Figures III-25, III-26) show that the polyaniline surface is partially covered with such crystals. It is most probable that ammonium chloride on the surface does not lead to any additional resistance against permeating gases, but it is problematic to quantify the effect of those depositions within the membrane matrix due to the fact that in a dense membrane no visible pores are present.
Change of permeation range by doping

Table IV-14: Permeation of hydrogen through a PANi / PVDF membrane and change of transport rates (cf. also Figure IV-21)

<table>
<thead>
<tr>
<th>Curve No</th>
<th>Time span /s</th>
<th>Slope of p vs. t curve / mbar/s</th>
<th>Permeability $10^{-4}$ Nm³/ bar h m²</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>60-200</td>
<td>0.0009</td>
<td>6.1</td>
<td>&quot;As-cast&quot; membrane</td>
</tr>
<tr>
<td>2</td>
<td>260-500</td>
<td>0.0004</td>
<td>2.7</td>
<td>Feed enriched with HCl (bubbled through conc. HCl)</td>
</tr>
<tr>
<td>3</td>
<td>650-1000</td>
<td>0.0005</td>
<td>3.4</td>
<td>Feed enriched with NH₃ (bubbled through 1M NH₄OH)</td>
</tr>
</tbody>
</table>

Table IV-15: Permeation of hydrogen through a PANi / PVDF membrane and change of transport rates (cf. Figure IV-22)

<table>
<thead>
<tr>
<th>Curve No</th>
<th>Time span /s</th>
<th>Slope of p vs. t curve / mbar/s</th>
<th>Permeability $10^{-4}$ Nm³/ bar h m²</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>60-250</td>
<td>0.0005</td>
<td>3.4</td>
<td>Membrane, HCl-doped</td>
</tr>
<tr>
<td>2</td>
<td>260-650</td>
<td>0.0007</td>
<td>4.7</td>
<td>Feed enriched with NH₃ (bubbled through 1M NH₄OH)</td>
</tr>
<tr>
<td>3</td>
<td>780-800</td>
<td>0.0005</td>
<td>3.4</td>
<td>Feed enriched with HCl (bubbled through conc. HCl)</td>
</tr>
<tr>
<td></td>
<td>800-1000</td>
<td>0.0005</td>
<td>3.4</td>
<td>Permeation of &quot;pure&quot; hydrogen</td>
</tr>
</tbody>
</table>

The experiments performed demonstrate the possibility of creating switchable polyaniline-based membranes.

Additional XPS examination could give more information on how deep the anions are incorporated into the polyaniline surface and how much chloride can be removed from the membrane with a doping / dedoping process as described above.

8.2 Permeability of polyaniline / PVDF composite membranes in different doping states

The experiments conducted started with the as-cast modification. For doping and dedoping, hydrogen was bubbled through an aqueous solution of concentrated ammonium-hydroxide (25%) and concentrated hydrochloric acid (40%), respectively. Then the HCl- and NH₃- enriched gas was passed over the membrane.

In order to dope the membrane, it was exposed to a gas stream of hydrogen (120ml/min for 4 minutes) enriched with HCl, as discussed in Chapter IV-8.1. In order to dedope the membrane
the same procedure was performed again after having replaced the acid by aqueous ammonium-
hydroxide.

With the membrane doped or dedoped this way, the test cell was evacuated again and the per-
meability of the four test gases (H₂, O₂, CO₂ and N₂) was determined for each exchange state at
a given pressure (cf. Figures IV-23 and IV-24). This way the permeability of the as-cast mem-
brane was determined, followed by permeation tests on doped and undoped membranes.

After several doping and dedoping processes, the feed side of the membrane was covered surfi-
cially with NH₄Cl crystals that precipitated from the ionic reaction of HCl gas with NH₄OH.

The partial pressures of HCl(g) and NH₃(g) over water are quite high: 525mbar in the case of
HCl and about 490mbar in the case of NH₃ at equilibrium conditions. In the experiments conducted a constant gas flux (hydrogen in this case) reduces the vapour pressures above the aqueous solutions.

In order to estimate the contribution of the vapours to the total pressure, a simple experiment
was carried out: during a permeation experiment a gas wash bottle, filled with ammonium hy-
droxide solution was introduced into the gas feed line and after a while removed. This proce-
dure was repeated more than 10 times.

The resulting permeation plot did not show any significant change of slope, although the ex-
perimental setup allows to measure pressure changes (in the feed stream) smaller than approxi-
mately 80mbar.

These experiments give an idea of the partial pressures of the vapours that passed over the
membrane simultaneously with hydrogen.

For future experiments, e.g. for doping with HCl, the gas concentration should be controlled by
the means of flow meters. This way a known amount of HCl gas can be introduced into the hy-
drogen feed line.

Figure IV-23 shows the permeability of the gases H₂, O₂, CO₂, and N₂ as a function of the dop-
ing state: as-cast (undoped), doped, and (partially) dedoped. In Figure IV-24, the ideal separa-
tion factor of the membrane is shown as a function of the membrane state.

The as cast membrane had the best performance concerning separation factor, followed by the
doped membrane.

Figure IV-23 also illustrates that the order of permeability is H₂ > O₂ > CO₂ > N₂, had been as
expected from previous results. Interestingly, the order of permeability is: as-cast > dedoped >
doped. This is in contradiction to the permeabilities measured in Chapter IV-6.6.1
Change of permeation range by doping

Figure IV-23: Gas flux through a PANi / PVDF membrane; \( A_M = 2.55 \text{cm}^2, t_{\text{PANI}} = 2 \mu\text{m}, p = 1.5\text{bar} \)

Figure IV-24: Ideal separation factors for PANi / PVDF membranes in different exchange states; doping and dedoping with gaseous HCl and NH₄OH
The same explanation as in IV-8.1 may apply: incomplete dedoping causes a residual amount of chloride in the membrane and affects the transport rate. This explains the reduced permeability as the transport rate directly depends on the doping level\textsuperscript{6}.

In the case of gas pairs containing nitrogen, the dedoped membranes have the smallest selectivities. The gas pair H\textsubscript{2}/CO\textsubscript{2} has the highest selectivity in the dedoped state, followed by the doped state and the as-cast state. In general, the highest gas permeability was exhibited by the as-cast membrane.

It is also interesting to discuss the influence of doping time on the degree of ion exchange. Up to now no publications exist in which the kinetics of gas-phase doping are investigated. Kuwabata et al.\textsuperscript{6} pointed out a relationship between conductivity (as an indirect indicator of doping) and exposure time to HCl vapour. One important question still remains unanswered: what time is required for a certain extent of doping at an arbitrary point inside the membrane matrix?
Temperature and pressure-related influences on gas permeability and selectivity

Temperature and pressure (concentration) both have a major influence on polymer permeability. In the following sections, pressure and temperature-related effects on gas transport are presented.

9.1 Permeability, separation factor and diffusion coefficient as functions of feed pressure

Figure IV-25 shows the permeabilities of the gases H₂, CO₂, O₂ and N₂ through as-cast polyaniline membranes as a function of the upstream pressure. As described in Chapter I-2.1, the impact of pressure on permeability gives information on the sorption mode and transport mechanisms of polymers.

Figure IV-25: Permeability of a PAni / PVDF membrane as a function of upstream pressure, $A_M = 7.1 \text{ cm}^2$

In Figure IV-26 the separation factors for the gas pairs are plotted as functions of feed pressure. The data were obtained by examining the pressure ranges 1 to 5.5 bar.
It can be seen that there is no clear evidence of any kind of pressure dependence (i.e. concentration dependence) of the permeability of hydrogen and nitrogen, but pressure may have a small influence on the permeability of oxygen (cf. standard deviation Table IV-16). Also CO₂ appears to permeate somewhat faster with increasing feed pressure.

The tendency for CO₂ permeation can also be seen: from the separation factors for gas pairs that contain carbondioxide tend to increase with rising pressure, whereas the separation factors for the other gas pairs are more or less constant (cf. Table IV-16).

This observation is substantiated by a statistical comparison. The data presented in Tables IV-16 and IV-17 show the standard deviation of individual rows (mean variation between individual values and mean value of a row). This deviation values indicate the influence of the feed pressure on permeability.

The statistics also indicate pressure dependencies if we compare the standard deviations of the permeabilities and separation factors.

The pressure dependencies follow the order CO₂ > O₂ > N₂, which reflects the order of permeability of these gases through polyaniline as found by other researchers (cf. Table IV-10).

Deviations from ideal behaviour can be observed for CO₂. Pressure dependence indicates a non-ideal behaviour in the diffusion process, even if the observed effect is small.
Temperature and pressure-related influences on gas permeability and selectivity

Table IV-16: Statistical overview of the pressure dependence of permeability data (in $10^3$ Nm$^3$/bar h m$^2$; (cf. Figure IV-25)

<table>
<thead>
<tr>
<th>Gas Pair</th>
<th>Pressure / bar</th>
<th>MV</th>
<th>St. dev. / %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>1.75</td>
<td>2.5</td>
</tr>
<tr>
<td>H$_2$</td>
<td>0.409</td>
<td>0.409</td>
<td>0.0416</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0.110</td>
<td>0.116</td>
<td>0.122</td>
</tr>
<tr>
<td>O$_2$</td>
<td>0.0262</td>
<td>0.0248</td>
<td>0.0244</td>
</tr>
<tr>
<td>N$_2$</td>
<td>0.0083</td>
<td>0.0079</td>
<td>0.0080</td>
</tr>
</tbody>
</table>

Table IV-17: Statistical overview of the pressure dependence of separation factors (cf. Figure IV-26)

<table>
<thead>
<tr>
<th>Gas pair</th>
<th>Pressure / bar</th>
<th>MV</th>
<th>St. dev. / %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>1.75</td>
<td>2.5</td>
</tr>
<tr>
<td>H$_2$/CO$_2$</td>
<td>3.7</td>
<td>3.5</td>
<td>3.4</td>
</tr>
<tr>
<td>H$_2$/O$_2$</td>
<td>14.9</td>
<td>16.6</td>
<td>17.1</td>
</tr>
<tr>
<td>H$_2$/N$_2$</td>
<td>51.5</td>
<td>51.9</td>
<td>51.5</td>
</tr>
<tr>
<td>CO$_2$/O$_2$</td>
<td>4.0</td>
<td>4.7</td>
<td>4.9</td>
</tr>
<tr>
<td>CO$_2$/N$_2$</td>
<td>13.9</td>
<td>14.7</td>
<td>15.1</td>
</tr>
<tr>
<td>O$_2$/N$_2$</td>
<td>3.5</td>
<td>3.1</td>
<td>3.0</td>
</tr>
</tbody>
</table>

If polyaniline is considered to be a glassy polymer under the conditions described Lee et al. and Lesueur et al. found $207^\circ$C and $200^\circ$C, respectively, for the glass transition temperature $T_g$, the permeability will decrease with increasing pressure due to compaction of the polymer.

At the same time the pressure reduces available space for the permeating molecules. Against this background an increase of permeability can only be explained by the high solubility of CO$_2$ in the membrane, as CO$_2$ is a rather condensable gas compared to the other gases. These results indicate that solubility effects dominate over effects that are related to the free volume. This suggests that solution-diffusion is superimposed by a plasticising effect of CO$_2$.

In general, the Dual-mobility model predicts that the permeability of a glassy polymer decreases with increasing (upstream) pressure. However, the permeability of some polymers considerably starts to increase above a certain pressure. In this case it has been stated that CO$_2$ swells the polymer and loosens the membrane matrix, which can be phenomenologically observed as an increase of the permeant flux.

For oxygen, no clear tendency can be seen. It is uncertain if the variance of permeability data comes from solubility effects.
Temperature and pressure-related influences on gas permeability and selectivity

A remarkable result is the observation that the time to reach steady-state conditions of permeation for N\textsubscript{2} was up to more than 15 hours, dependent on the feed pressure. The thickness of the polyaniline layer in the composite membrane was just about 8µm.

The unsupported membranes that were tested by Chang \textit{et al.}, Kuwabata \textit{et al.}, Kaner \textit{et al.}, and by others\textsuperscript{1-6}, were 15-100µm thick (cf. Table III-2).

Provided that the time lag linearly depends on the membrane thickness, the researchers should have needed a time of about 15 to more than 60 hours to reach steady state; a time span much longer than the membranes have been tested.

One might think that these researchers did not measure for a sufficiently long time, until steady-state conditions were reached. In such cases the results are high separation factors for gas pairs containing nitrogen due to the obviously low permeability of that gas.

It is quite interesting that Rebattet \textit{et al.}\textsuperscript{4} report on time lags of less than 30 minutes.

A few potential factors that effect permeability are given by the variation of components in the polyaniline layer: different polymerisation agents (e.g. H\textsubscript{2}SO\textsubscript{4}, p-TSA or HCl for acidification) may result in different polymerisation rates and mass distribution in a way that the different polymerisation products may differ more or less in their properties. Research on this issue has not been published yet.

Also, the presence of NMP (see Chapter III-4.4) in the membrane may influence permeability due to interactions with the polymer or the gas, as swelling in general loosens the polymer matrix and therefore increases permeability.
9.2 Diffusion coefficient as a function of the feed pressure

In this section the diffusion coefficients for permeation through as-cast PANi / PVDF membranes are calculated using the time lag method. Figures IV-27 to IV-30 show \( p \) vs. \( t \) plots for the gases \( \text{H}_2, \text{CO}_2, \text{O}_2 \) and \( \text{N}_2 \). Each curve represents an average of 4 permeation tests. The thickness of the polyaniline layer was 8µm.

![Figure IV-27: \( p \) vs. \( t \) plot for \( \text{H}_2 \) permeating through an as-cast PANi / PVDF membrane](image)

The permeation plot for hydrogen does not show any time lag. In contrast to that for carbon dioxide and nitrogen have a detectable time lag. In the case of oxygen the extraordinarily thin polyaniline layer did not allow to identify reliable time lag data, whereas in the case of \( \text{CO}_2 \) and \( \text{N}_2 \) (cf. Table IV-18) a determination of the transition time was possible.

Even testing of comparatively thick membranes (up to 67µm, cf. Chapter IV-6.4.1) did not give any evidence of a time lag for hydrogen.
Temperature and pressure-related influences on gas permeability and selectivity

Figure IV-28: $p$ vs. $t$ plot for CO$_2$ permeating through an as-cast PAni / PVDF membrane

Figure IV-29: $p$ vs. $t$ plot for O$_2$ permeating through an as-cast PAni / PVDF membrane
Temperature and pressure-related influences on gas permeability and selectivity

A pressure-dependent diffusion coefficient indicates that the presence of the permeant changes the membrane properties e.g. by swelling, and that at the same time means high solubility for the gas in the membrane.

In the case of nitrogen no strong interaction with polyaniline is expected. An explanation for a pressure dependence of the diffusion coefficient is given by the Dual-mode mobility model (see Chapter I-2.3.3). The equation I-53 describes the concentration dependence of diffusion coefficients for glassy polymers, in the case of which the effective diffusion coefficient $D_{\text{eff}}$ increases with increasing permeant concentration. According to this model, at low concentrations the gas is dissolved in accordance with the Langmuir and Henry modes. Under these conditions both modes contribute to the total mobility of the gas. When concentration increases, the sites that are related to the Langmuir mode will by and by be saturated. At the same time the more mobile molecules that are sorbed in accordance with the Henry mode will increasingly contribute to the overall mobility of the penetrant.

Table IV-18: Diffusion coefficients ($D \cdot 10^{10} \text{cm}^2/\text{s}$) for $N_2$ and $CO_2$ at various pressures determined by the time lag method

<table>
<thead>
<tr>
<th>Gas</th>
<th>Pressure / bar</th>
<th>1</th>
<th>1.75</th>
<th>2.5</th>
<th>4</th>
<th>5.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td></td>
<td>8.74</td>
<td>10.16</td>
<td>11.23</td>
<td>12.55</td>
<td>16.16</td>
</tr>
<tr>
<td>N$_2$</td>
<td></td>
<td>0.053</td>
<td>0.08</td>
<td>0.323</td>
<td>1.065</td>
<td>1.445</td>
</tr>
</tbody>
</table>

Figure IV-30: $p$ vs. $t$ plot for $N_2$ permeating through an as-cast PAni / EB / PVDF membrane
9.3 Permeability and separation factor as functions of temperature

Temperature is an important parameter that directly affects physical properties of the membranes. Transport through dense membranes is considered an activated process and is usually expressed by an Arrhenius-type equation. The temperature dependence of permeability and separation factor can be explained as the sum of sorption enthalpy and activation energy.

The Arrhenius plot in Figure IV-31 allows the calculation of the activation energy $E_p$ for permeation. In order to determine the activation energy, the curves were fitted to the data using a linear least-squares approach. The activation energies of permeation are listed in Table IV-19, as well as data of other researchers for comparison.

Figure IV-31: Arrhenius plot; permeation of various gases through an as-cast PANi / PVDF membrane; $A_M = 7.1 \, \text{cm}^2$, $t_M = 8.4 \, \mu\text{m}$, $P_{\text{Feed}} = 2.5 - 3 \, \text{bar}$, $\ln P \, (\text{Nm}^3/\text{bar \cdot h \cdot m}^2)$

Figure IV-31 shows the Arrhenius plot for the four tested gases in the temperature range of 25°C up to 65°C. The $\ln P$ vs. $1/T$ curve for each gas gives the slope $E_p/R$ to calculate $E_p$ (cf. eq. I-36). In the present work, linear relationships were found from Arrhenius plots of the permeability.

The space needed by the permeating molecules is related to its kinetic diameter (cf. Table IV-21). Many researchers relate polyaniline permeability to the kinetic diameters of the passing
Temperature and pressure-related influences on gas permeability and selectivity

Gases\(^5,17\). Gas molecules can pass through transient gaps in the polyaniline matrix that are equal to or larger than their effective size.

In general, differences in the activation energies are related to the required amount of energy to overcome the thermally agitated motion of polymer chain segments during the diffusion process\(^18\).

As can be seen in Table IV-19, the order of the activation energy for permeation \(E_p\) through PANi / PVDF membranes is \(E_p\) CO\(_2\) \(<\ E_p\) H\(_2\) \(<\ E_p\) O\(_2\) \(<\ E_p\) N\(_2\).

The order \(E_p\) CO\(_2\) \(<\ E_p\) H\(_2\) is remarkable in so far as the published data differ. The lower activation energy for CO\(_2\) (compared to hydrogen) implies that the solubility of CO\(_2\) has a high influence on its permeability through composite membranes, and this solubility is likely to be responsible for the observation made.

Due to the fact that high activation energies are associated with lower permeability coefficients the order of permeability is the reverse of that of the activation energies except for CO\(_2\), which permeates more slowly than hydrogen.

It was also found that the activation energy for permeation \(E_p\), is generally higher than some published data, especially compared to the results published by Anderson\(^1\). On the basis of these results the activation energy according to Anderson was calculated by using the relation

\[
E_p = E_D + \Delta H_S \tag{IV-1}
\]

with

\[
\begin{align*}
\Delta H_S & \text{ solution enthalpy (kJ/mol)} \\
E_D & \text{ activation energy for diffusion (kJ/mol)}
\end{align*}
\]

It is interesting to mention that Anderson measured permeability only at three different temperatures (cf. Table IV-19). This might have been a potential source of inaccuracy.

Our tests were performed on comparatively thin as-cast polyaniline membranes with a thickness of only 8.4\(\mu\)m, whereas the activation energies published by Chang \textit{et al.}\(^5\) and calculated for Anderson were obtained with tests on much thicker membranes (100\(\mu\)m).

As shown by IR-studies (Lux\(^19\), and own examinations, see Chapter III-4.4), as-cast membranes still contain a residue of NMP. It could be argued that more NMP might be present the in a thick film than in a much thinner film, produced in the same way (or exposed to higher temperatures during the curing process).
Temperature and pressure-related influences on gas permeability and selectivity

The presence of such a swelling agent may loosen the chain segments in a way that the polymer chains become more flexible and so that the energy needed for a gas to pass the polymeric matrix is reduced.

The other membrane exchange states can not be directly compared to the as-cast state, because the incorporation or removal of anions causes an elimination of NMP, as well as structural changes within the membranes.

X-ray diffraction studies on thick and thin films may provide evidence as to whether the number of amorphous sites declines with reducing film thickness, or if alternatively the interchain alignment becomes more ordered. Such an increase of crystallinity (coupled with a higher rigidity of the polymer chains) could be an explanation for higher activation energies required for thin films.

Table IV-19: Apparent activation energy (E_p/kJ/mol) for permeation through unsupported PANi membranes and polyaniline based composite membranes

<table>
<thead>
<tr>
<th>State</th>
<th>As cast</th>
<th>As cast*</th>
<th>HCl doped</th>
<th>Dedoped*</th>
<th>Redoped</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane type</td>
<td>PANi / PVDF</td>
<td>unsupported</td>
<td>unsupported</td>
<td>unsupported</td>
<td>unsupported</td>
</tr>
<tr>
<td>Examiner</td>
<td>own</td>
<td>Chang et al.</td>
<td>Anderson</td>
<td>Chang et al.</td>
<td>Anderson</td>
</tr>
<tr>
<td>T-range/°C</td>
<td>25 - 65</td>
<td>19 - 60</td>
<td>33 - 75</td>
<td>19 - 60</td>
<td>33 - 75</td>
</tr>
<tr>
<td>Gas</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H2</td>
<td>27.55</td>
<td>20.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CO2</td>
<td>26.25</td>
<td>23.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>O2</td>
<td>39.15</td>
<td>23.8</td>
<td>8.6</td>
<td>-</td>
<td>7.9</td>
</tr>
<tr>
<td>N2</td>
<td>48.60</td>
<td>27.6</td>
<td>8.5</td>
<td>54.0</td>
<td>12.3</td>
</tr>
</tbody>
</table>

*calculated from published results by using eq. IV-2

If diffusion is considered to be "ideal", and provided that PVDF has a negligible effect on permeation through the polyaniline / PVDF material, the permeation-related coefficients found should be due to the polyaniline layer only.

The linearity of the curves (cf. Figure IV-31) proofs that no phase transition occurred within the polymer. Permeation changes due to the transition from the glassy to the rubbery state were outside the chosen temperature range.

Figure IV-32 gives information on the temperature dependence of the ideal separation factors that are based on the permeabilities measured before.
Temperature and pressure-related influences on gas permeability and selectivity

The permeation selectivity decreases with rising temperature, except for one gas pair H₂/CO₂. Interestingly, the separation factor of that gas pair hardly depends on the temperature, whereas it significantly decreases with rising temperatures in the case of all other gas pairs.

This result is quite remarkable because hydrogen is a molecule that cannot be proofed to be soluble in polyaniline, and publications on hydrogen sorption on polyaniline have not been published yet. On the other hand, carbon dioxide permeates readily, being a representative of a quite soluble species in polyaniline. Thus in contrast to hydrogen the solubility of CO₂ is significantly dependent on temperature.

![Figure IV-32: Ideal separation factor for various gas pairs for as-cast PAni/PVDF membranes at T 298-338K; A_M = 7.1 cm², t_M = 8.4µm, p_Feed = 2.5-3bar.](image-url)
10 Differential pressure method

The time lag method and the CVVP method are well established techniques to measure membrane permeability.

However, the differential pressure method as described in Chapter II-3.1.9.3 offers an interesting alternative to the established time lag method. Before the discussion of the permeation results found with this method some general statements shall be made about limitations, but also about advantages of this test method:

Maintaining atmospheric pressure as a constant reference pressure sometimes causes problems, because small pressure changes influence the results. This may increase the variation of the pressures measured, in particular in the case of slowly permeating gases such as nitrogen. The composition of the atmosphere on the downstream side must be also considered; especially the partial pressure of the permeating gas, because the driving force for permeation of a single gas is defined as the pressure difference of the partial pressures of the gases in the upstream and the downstream volume.

Effects caused by rediffusion of residue gases into the test atmosphere were observed, indicated by a pressure drop in the downstream volume. The facts mentioned above do thus contribute limitations to the precision of results obtained with this method.

Nonetheless, it offers some significant advantages over conventional permeation testing methods:

1) There is no need for a vacuum system. That means that the diffusion cell must not be evacuated overnight in order to minimise the effect of desorbing gases. For permeation measurements it is required to wait until steady-state conditions within the membrane have been established.

2) Another quite important point is that several tests with one and the same gas can be conducted directly one after the other without pausing, which usually is required for evacuation.

3) Furthermore, the samples can be tested under atmospheric conditions. Standard permeation tests use idealised conditions with a vacuum on the downstream side and overpressure on the feed side. In real applications, overpressure on the feed side is not automatically coupled with a vacuum on the downstream side. This means e.g. that sites already occupied at high pressures in the polymer structure may affect permeability.
4) Physical effects like counter-diffusion can be observed directly, e.g. in the case of hydrogen permeating into a nitrogen atmosphere. Such experiments are interesting when studying the interaction between the permeating species during the permeation process.

10.1 Permeation tests performed using the differential pressure method

Steady-state permeation is reached when parallel $p$ vs. $t$ curves are obtained. For slowly permeating gases such as nitrogen this may result in the need for several hours of operation until steady-state is reached.

Figures IV-33 and IV-34 show two example permeation plots for the permeation of N$_2$ and H$_2$, respectively. The sawtooth-like curves make the operation of the test method visible: a relative increase of the pressure on the downstream side. If a constant flux rate is achieved, the slope of the $p$ vs. $t$ curve becomes constant. The release of the overpressure into the atmosphere is then indicated by a pressure drop to "zero".

![Permeation plot of N$_2$ permeating through a PAni / PVDF membrane, $A_M = 12cm^2$, $p_{Feed} = 5bar$.](image.png)

The use of this test method yielded remarkable results. Figure IV-35 shows the separation factor for various gas pairs. As can be seen, the highest ideal separation factor is about 30 in the case of H$_2$/N$_2$, and the lowest was obtained for the gas pair O$_2$/N$_2$ (about 2). Interestingly, the separation factors for gas pairs containing nitrogen are significantly below those calculated...
from the permeabilities in Chapter IV-7.2, whereas the separation factors for the other gas pairs are comparable with each other.

One explanation for these results might be that the gas flux in the time lag experiments did not reach steady-state conditions. This argument might be substantiated by taking another look at Figure IV-30: this permeation plot was obtained from permeation tests in which the membranes were subjected to different nitrogen pressures. Steady-state diffusion through the 8µm-thick polyaniline layer was not reached before more than 15 hours at a feed pressure of 1bar. In these time lag experiments the separation factors for gas pairs containing nitrogen (i.e. (H₂/N₂=51.9 or CO₂/N₂=13.9) were below those calculated in the other permeation tests (CVVP method and diffusion cell), but they are higher than those determined by the differential pressure method. Supposingly even the extraordinarily long duration of the time lag tests (more than half a day) still may not be sufficiently long to ensure steady-state permeation.

Compared to the results obtained by Rebattet et al.⁴ who measured a time lag of less than 30 minutes, this is quite a notable result. Another interesting observation made also was, that tests performed with the CVVP method (see Chapter II-7.3) showed an increase of permeability with the number of tests made in succession. The observed increase of permeability indicates that steady-state diffusion had not been reached when the permeation tests were stopped.

Figure IV-34: Permeation plot of permeating hydrogen through a PANi / PVDF membrane, A_M = 12cm², p_Feed = 5bar
In the case of nitrogen permeation, counter-diffusion was observed if a residue of hydrogen had remained in the downstream part: even nitrogen overpressures of 5 bar did not result in an increase of the downstream pressure. On the contrary: As long as hydrogen was present in the downstream volume, the differential pressure was declining, caused by a diffusion of molecules from the downstream part into the upstream part. This observation illustrates that the permeation rate of the individual gases in gas mixtures depends on the individual partial pressures.

It is difficult to assess the influence of the simultaneous presence of various gases on permeability. In some strongly interacting polymer-permeant systems, permeation of a second gas present was suppressed. Sanders et al. \(^{20}\) report on exclusion of CO\(_2\) from Langmuir sorption sites in poly(methyl methacrylate), PMMA, as ethylene partial pressure is increased in the presence of CO\(_2\) at a constant partial pressure.

With the differential pressure method such observations have not been made as yet. This is due to the non-availability of technical equipment, not the method itself.

The installation of a high-accuracy pressure sensor in the upstream part should allow to measure the direction and quantity of gas flux. Additionally, GC-MS technique could then also be used to examine the composition of the mixed gases in the corresponding volumes.

Figure IV-35: Ideal separation factors for various gas pairs permeating through a PANi / PVDF membrane
11. Comparison of experimental and calculated permeation data

In this section, the experimental permeation results and the calculated permeabilities will be compared. According to the solution-diffusion model, the permeability is calculated according to the equation

\[ P = D \cdot S \]

Besides solution-diffusion, gas transport can also occur according to the Dual-mobility model. This model describes diffusion through glassy polymers for which the assumption of a concentration-independent diffusion coefficient does not apply, if two kinds of gas molecules exist: mobile molecules that are dissolved according to the Henry mode, and an immobilised portion that is sorbed according to the Langmuir mode.

In the present work, the coefficients for the Dual-mobility model could have only have been calculated precisely if permeation data over a wide pressure range had been available. Only in sorption experiments related to the different modes could be observed at higher pressures. Especially when slowly permeating gases were involved, the measured effects were beyond measurement resolution of the diffusion cell which worked very accurately at pressures up to 6bar, but showed sealing and leakage problems at feed pressures above 6bar.

In the following, the permeability is calculated by using the equation \( P = D \cdot S \), where the solubility \( S \) was calculated from the BET model, Langmuir sorption (LA), or the Dual-mode model (DM). The experimental permeability data (Exp.), as well as the data that were obtained from the models are listed in Table IV-20 and the experimentally determined data for the diffusion coefficients are listed in Table IV-18.

Table IV-20: Permeability \( P \) (Barrer), calculated from Dual-mode sorption (DM), Langmuir (LA), and BET isotherms, compared to experimental permeability data

<table>
<thead>
<tr>
<th>Pressure/ bar</th>
<th>( P_{CO_2} )</th>
<th>( P_{N_2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( D \cdot S ) (BET)</td>
<td>( D \cdot S ) (DM)</td>
</tr>
<tr>
<td>1</td>
<td>0.9256</td>
<td>0.3657</td>
</tr>
<tr>
<td>2.5</td>
<td>0.6909</td>
<td>0.1880</td>
</tr>
<tr>
<td>5.5</td>
<td>0.5602</td>
<td>0.1229</td>
</tr>
</tbody>
</table>

*Data for the diffusion coefficients are listed in Table IV-18*
Comparison of experimental and calculated permeation data

It can generally be stated that the calculated permeability data for CO₂ correspond with the experimentally obtained data.

If the Dual-mode model and the BET model (at pressures below 35 bar) are taken to describe sorption, under the premise that the diffusion coefficient is pressure-independent, the permeability will decrease when pressure rises. This result is in opposition to the experimental data, which show an increase of permeability with rising feed pressures. This suggests that solution-diffusion is superimposed by a plasticising effect of CO₂ as discussed in Chapter IV-5.2.

Another interesting result was obtained for the calculated permeability of nitrogen at 1 bar: the permeability is almost ten times smaller than the experimentally measured permeability. The calculated data at 1 and 2.5 bar is below, and permeability at 5.5 bar is of the same magnitude as the experimental data.

Within the range of 1-5.5 bar sorption of nitrogen almost depends linearly on the pressure (cf. Figure IV-5). That means that only a pressure dependent diffusion coefficient can be made responsible for the observation made.

A pressure-dependent diffusion coefficient is an indication that the presence of the permeant changes the properties of the membrane, e.g. by swelling. If swelling takes place in the presence of a permeant it normally means that the permeant is highly soluble in the membrane. Neither swelling nor high solubility was found in the case of nitrogen. The solution-diffusion equation \( P = D \cdot S \) seems to be inapplicable to calculate the permeability of nitrogen. More experimental data especially gained at a wider pressure range could help to explain this phenomenon.

It is important to mention that sorption was determined for polyaniline powders, whereas the solution-diffusion equation is valid membranes. It is possible that only sorption data obtained from experiments on polyaniline films can be used to calculate permeability. Comparing the sorption of nitrogen and oxygen (cf. Figures IV-4 and IV-5) one can see that the sorption of nitrogen is less than a half of that of oxygen, whereas the permeation selectivity (the ideal separation factor) is 7 to 10 (cf. Table IV-13).

These results give evidence that the selectivity may be influenced by Dual-mobility diffusion. It might also be possible that the diffusional access of these gases to the polymer structure is dependent on the size of the permeant (cf. Table IV-21) and the structure favours smaller molecules over larger molecules.
Table IV-21: Kinetic diameters of oxygen and nitrogen according to Breck$^{21}$

<table>
<thead>
<tr>
<th>Gas</th>
<th>Kinetic diameter / $10^{-10}$ m</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_2$</td>
<td>3.46</td>
</tr>
<tr>
<td>N$_2$</td>
<td>3.64</td>
</tr>
</tbody>
</table>

The latter statement is backed by investigations of Pellegrino et al.$^{22}$ who found evidence that the accessible free volume can be changed by doping and dedoping the film so that ion exchange can create molecular-selective conditions. This implies that accessible sites and structures are present within the polymer matrix and that they can be modified.

Studies of Wessling et al.$^{23}$ on thinnest polyaniline layers may substantiate these observations. SEM examinations revealed structures that had a morphology similar to that of sintered globules of 50-100nm diameter. STM examinations, also performed by Wessling et al., give evidence of the existence of spherical particles with a diameter of just about 5-15nm. These structures found with smallest interstices can supposedly work like sieve.

the existence of such structures in the membranes tested could be an additional factor that has to be considered additional to the models discussed when assessing permeation properties.
12 Conclusions

Polyaniline-based membranes were developed during this work. The combination of polyaniline with polymeric support materials offers the opportunity of creating large, dense and stable membrane areas in a quite simple and reproducible way.

Doping and dedoping with HCl changes the gas permeability and selectivity and makes it possible to change the separation efficiency by controlled ion exchange.

Furthermore, the present work shows the usability of polyaniline membranes for the production of large and dense films: unsupported membranes with areas of 13 x 18 cm were reproducibly produced by casting polyaniline dispersions onto glass plates and evaporating the solvent. Even larger membranes made that way meet the requirement of being defect-free.

The creation of polyaniline-based composite membranes is a big step forward coping with problems that arise in the production of large membrane areas. Combined with PVDF, those composites are promising materials to achieve the high selectivities, desired. By simultaneous reduction of the film thickness the permeation rate can be increased by at least 5 times compared to the data in other publications.

The thickness of such membranes could be reduced down to 1.6 µm, approximately 2 to 50 times thinner as compared to data reported by other researchers.

The separation factors for the interesting gas pairs H₂/CO₂ (3.5), CO₂/CH₄ (40) and O₂/N₂ (7) surpass the selectivities of the majority of conventional polymeric materials.

Thinnest polyaniline layers on PVDF supports allowed the observation of permeation change during doping and dedoping the membranes. It has also been illustrated in how far the gas flux responds to doping. In these tests, the change of permeability was observed in situ for the first time ever.

The application of coatings based on polysiloxane is another big advantage with respect to simplifying membrane production. Smallest microporous defects can be plugged in a simple way without affecting the polyaniline layer itself, and still maintaining selectivity. The combination of polyaniline / PVDF with siloxanes allows plugging microscopic defects without restricting the permeant flux, in a way that the largest available defect-free membrane area is no longer determined by the number of microporous defects.
Conclusions

Also ceramic materials were coated with polyaniline. The great advantage of ceramic support materials is the high mechanical stability combined with the resistance against solvents. Besides application in the field of gas-separation, the combination of polyaniline with ceramic materials offers some prospects for the separation of liquid mixtures of solvents, or separation by pervaporation.

During the present work, the composite materials created were compared with unsupported polyaniline membranes. The gas flux was found to be directly proportional to the thickness of the polyaniline layer.

Extraordinarily high time lag values were found for polyaniline / PVDF membranes which underlines the necessity of sufficiently long durations of the permeation tests.

Validation tests with the CVVP method proved to coincide the result obtained in this work.

Sorption tests were performed in pressure ranges that had not been tested before. In the case of oxygen, the Dual-mode model was found to be appropriate to describe sorption, whereas sorption on nitrogen could satisfactorily be described by the Langmuir isotherm.

Isotherms of carbon dioxide indicate that the Dual-mode model applies at pressures up to 35bar. Multi-layer sorption and condensation at still higher pressures can be described by the BET model.

In the case of nitrogen, diffusion coefficients were determined that are by some orders higher than those observed by other authors.

Carbon dioxide permeability through the polyaniline / PVDF membranes was found to be increasing with rising feed pressures. Such behaviour can be explained by plasticising effects of the permeant.

In the case of nitrogen, the Dual-mode model could not be applied to sorption, whereas the Langmuir sorption model was proofed to be a good approach. For oxygen, sorption according to the Dual-mode model was found.

In the case of nitrogen, gas transport seems to additionally depend on size exclusion within a nanoporous material, besides on sorption of the gas in polyaniline.

Globule-like structures of ultrathin polyaniline layers as found by Wessling et al., also give reason to assume a sieving mechanism that is responsible for nitrogen separation.
12 Future work

The introduction of a production technique designed to produce large membrane areas in a continuous process is a major aim to reduce membrane production costs. Instead of solution casting, one should think about dip-coating or related production techniques.

Besides the combination of polyaniline with porous support materials such as PVDF, also the use of ceramic materials offers interesting alternatives. Large surface areas can be realized by using ceramic tubes and their combination to large membrane modules.

The comparison of ideal and real separation factors should give insight into competitive permeation within the membranes. Therefore it is of interest to compare gas mixtures and real separation factors e.g. by using mass spectroscopy techniques. This would be a step forward into the direction of developing a model that describes diffusion of individual gases, as well as simultaneous diffusion of gas mixtures in polyaniline membranes.

At the end of this work, a new measurement technique was introduced to measure a gas transport under atmospheric conditions more realistically. It was found that the permeability of some gases differs from the coefficients determined by means of the well-established time lag method; an important observation with respect to separation of gas mixtures and the determination of the real separation factor.

More information on permeation at higher pressures (> 6bar) requires the development of a high-pressure permeation apparatus that works at pressures up to 70bar. Such high-pressure permeation data are required to find a permeation model that covers the whole pressure range from 0 up to 70bar of feed pressure.

Another interesting option is the production of switchable membranes. Studies at Daimler-Benz Aerospace at the beginning of the 90's concerning the application of polyaniline in so-called "smart windows"\textsuperscript{24,25} raised the interest to create "smart membranes": in switchable optical devices, polyaniline served as a storing layer for anions, and the corresponding cations were used to color tungsten(VI)-oxides. Incorporation or removal of ions was achieved by applying an electrical potential between the two layers.

An interesting consideration is to create a multilayer membrane based on the above-mentioned technology to create switchable membranes which change selectivity and permeant flux only by a change of the polarity of the applied voltage.
1. Gas outlet or vacuum
2. Upstream volume
3. Gas feed
4. Vacuum line
5. Downstream volume
6. Pressure sensor
Appendix

Sorption Apparatus

1. Pressure sensor 1
2. Sample volume \( (V_1) \)
3. Thermostat
4. Gas volume \( (V_2) \)
5. Pressure sensor 2
6. Display sensor 1
7. Display sensor 2
8. Controller of syringe pump
9. Vacuum line
Appendix

Differential Pressure Cell

1. Gas feed
2. Differential pressure sensor
3. Upstream part of diffusion cell
4. Downstream part
5. Ventilation
6. Pressure sensor for downstream part (optional)
7. Gas outlet
8. Display, differential pressure sensor
The BET isotherm

Brunauer, Emmett and Teller derived a relationship between the pressure of a given gas and the adsorbed amount of it from a gas-kinetic and a statistic model for the physisorption of gases. The BET equation considers the amount of different layers filled to different extent, before the first (mono)-layer is completely filled. The BET theory includes the simplification, that the adsorption energies, the kinetic constants, the equilibrium of evaporation and condensation are the same in the higher layers, the adsorption energy is the same as the condensation energy, and that the probability of adsorption at a certain site does not depend on the coverage of the neighbouring sites. The classification of adsorption isotherms, adsorption hysteresis and the different models to calculate (or assess) the pore size distribution of mesoporous and microporous materials, and the limitations of the models are described explicitly in the literature\textsuperscript{26,27,28,29}. The BET-isotherm is commonly expressed as:

\begin{equation}
\frac{p_r}{(1-p_r) \cdot V} = \frac{1}{c \cdot V_{\text{mon}}} + \frac{(c-1) \cdot p_r}{c \cdot V_{\text{mon}}} \tag{IV-3}
\end{equation}

The coefficient that is related to the coverage $V_{\text{mon}}$, and the BET constant $c$ can be determined by graphical means:

\begin{align*}
m &= (c - 1) / c \cdot V_{\text{mon}} \\
b &= 1 / c \cdot V_{\text{mon}}
\end{align*}

with

- $p_r$ = relative pressure
- $p$ = pressure
- $p^\ast$ = gas pressure under ambient conditions
- $V$ = adsorbed gas volume at equilibrium pressure
- $V_{\text{mon}}$ = volume of the mono layer
- $C$ = BET constant, includes $\Delta H_{p,\text{ad}}$ and $\Delta H_{p,c}$

\begin{align*}
\text{\textbullet} & p_r \quad \text{p/p* = relative pressure} \\
p & \quad \text{pressure} \\
p^\ast & \quad \text{gas pressure under ambient conditions} \\
V & \quad \text{adsorbed gas volume at equilibrium pressure} \\
V_{\text{mon}} & \quad \text{volume of the mono layer} \\
C & \quad \text{BET constant, includes $\Delta H_{p,\text{ad}}$ and $\Delta H_{p,c}$}
\end{align*}
The Langmuir isotherm

The Langmuir adsorption isotherm includes the following assumptions: the surface is essentially homogeneous (identical composition and appearance everywhere). The surface has only a specific number of sites. Each of them can adsorb only one molecule. When these sites are all occupied, no further adsorption can occur, and the surface has achieved saturation (i.e. a monolayer of adsorbate). Furthermore, all sites are considered to be equivalent in a way that the energy of an adsorbed molecule is independent of the presence of other molecules.

The Langmuir adsorption isotherm can be expressed by the equation

\[
\frac{p}{c_H} = \frac{p}{b'} + \frac{1}{c_{H'} \cdot b'}.
\]

[IV-4]

where

- \(p\) pressure (bar)
- \(c_H\) adsorbed volume (cm\(^3\)STP/cm\(^3\))
- \(c_{H'}\) adsorbed volume at full coverage (cm\(^3\)STP/cm\(^3\))
- \(b'\) constant describing the affinity between pores and molecules (1/bar)

The plot \(p/V\) vs. \(p\) should give a straight line of gradient \(= 1/b'\), and an intercept \(= 1/c_{H'} \cdot b'\) with the y-axis:
Error Discussion

The guaranteed accuracy of the pressure transducers in this work is greater than 1% of the full detection range (e.g. pressure sensor MKS, range 0.001 - 10 mbar). The average leak rate of the diffusion cell used in this work was 0.018 mbar/h. This means that the leak rate of the diffusion apparatus was equivalent to a permeability of $1.95 \cdot 10^{-6}$ Nm²/bar-h-m² (or 0.0036 Barrer).

The estimated errors also vary with the magnitudes of the time lag and permeability. The estimated errors in gas permeability, diffusion coefficients, and activation energies for individual measurements are approximately 10% in the case of hydrogen and carbon dioxide, and up to 15-20% in the case of oxygen and nitrogen.

In order to calculate the permeability, the leak rate was subtracted from the measured permeation results.

The application of statistical methods and their application with respect to experimental data allowed to assess how exact the data were. Various statistical methods exist for that, which are explicitly explained e.g. by Linder and Petersen.

For permeation experiments it is interesting to obtain information on the deviation of data that is caused by experimental errors. A measure for this is given by the t-test: For an example, statistical tests allow to calculate the potential deviation of the data at a given probability. This deviation is called "confidence interval" (of the permeation data) and can be calculated by means of statistical tests based on the "t-distribution".

Exemplary for the measured permeability, the confidence level (or interval) $P = 0.95$ (meaning that with a probability of 95% the measured permeability is within the calculated range) can be determined as follows:

$$\mu' = \bar{x} \pm (t' \cdot S'/\sqrt{n'})$$

$$= 0.0759 \pm (2.447 \cdot 0.01765/2.6458) = 0.0759 \text{Barrer} \pm 0.0163 \text{Barrer}$$

with the coefficients

- $\bar{x}$: mean value; permeability (Barrer) of O₂ through a redoped membrane
- $S'$: standard deviation
- $n'$: number of tests
- $t'$: statistical parameter
- $\mu'$: real mean value
Appendix

Publications

G. Illing¹, K. Hellgardt¹, R.J. Wakeman¹, A. Jungbauer²

Journal of Membrane Science 184 (2001) 69-78

PREPARATION AND CHARACTERISATION OF POLYANILINE-BASED MEMBRANES FOR GAS-SEPARATION

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G. Illing¹, K. Hellgardt¹, A. Jungbauer²

in progress

POLYANILINE-BASED COMPOSITE MEMBRANES FOR GAS-SEPARATION

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26721 Emden, Germany
Appendix

Curriculum vitae

May 1989: school-leaving examination ("Abitur")

1989 - 1991 military service in Goslar, Wiesmoor and Hohenkirchen

1991 - 1996 studies of biotechnology at the University of Applied Sciences in Emden (FHO/O/W)

September 1994 - March 1995: 1st industrial training semester at Daimler-Benz Aerospace, Friedrichshafen / Germany

March 1996 - September 1996: 2nd industrial training semester at Daimler-Benz Aerospace, Friedrichshafen / Germany

October 1996: University of Applied Sciences leaving examination ("Diplom")

January – June 1997: participant in the EU-funded Leonardo student exchange programme at De Montfort University / Leicester

September 1997: begin of the dissertation at Loughborough University

September 2001: employment at Poly-Beek GmbH / Germany

August 2002: final examination for the degree "Doctorate of Philosophy" at Loughborough University
## List of Symbols

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<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
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<td>individual species A, B</td>
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<td>$b'$</td>
<td>microvoid affinity constant</td>
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<td>concentration dissolved (Henry)</td>
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<td>$G_p$</td>
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<td>$H_c$</td>
<td>Henry coefficient</td>
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<tr>
<td>HCl</td>
<td>hydrochloric acid</td>
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</tr>
<tr>
<td>i</td>
<td>kind of species</td>
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<tr>
<td>ICP</td>
<td>intrinsically conducting polymers</td>
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<td>$J, J_i$, $J_A$, $J_B$</td>
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<td>Symbol</td>
<td>Definition</td>
<td>Unit(s)</td>
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<td>(( \mu )m)</td>
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<td>( \ell_0 )</td>
<td>film thickness at beg. of transition range</td>
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<td>(kg)</td>
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<td>molecular weight of molecules A and B</td>
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<td>pressure</td>
<td>(Pa)</td>
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<td>pressure on upstream side</td>
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<td>( p_2 )</td>
<td>pressure in downstream volume</td>
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<td>gas pressure under ambient conditions</td>
<td>(mbar)</td>
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<td>( p_n )</td>
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<td>permeability, ( 7.4 \cdot 10^{-4} P(\text{Si}) )</td>
<td>(Barrer)</td>
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<td>(Barrer)</td>
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<td>pressure during determination of gas volume</td>
<td>(bar)</td>
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<td>( r_p )</td>
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<td>gas constant</td>
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<td>solubility coefficient</td>
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<td>standard deviation</td>
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<td>( T_c )</td>
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<td>Description</td>
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<td>$V_{\text{mon}}$</td>
<td>volume of the mono-layer (cm³)</td>
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<td>$V$</td>
<td>gas volume (cm³)</td>
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<tr>
<td>$V_A$</td>
<td>downstream volume (cm³)</td>
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<td>$x$</td>
<td>thickness of layer (cm)</td>
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<td>$Z$</td>
<td>collision frequency (1/s m³)</td>
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<td>$\alpha_c$</td>
<td>constant for concentration dependence</td>
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<tr>
<td>$\alpha$</td>
<td>ideal separation factor</td>
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<tr>
<td>$\bar{p}$</td>
<td>mean pressure within pore (Pa)</td>
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<td>$\bar{\eta}$</td>
<td>dynamic viscosity (Pa s)</td>
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<td>$\tilde{M}_1, \tilde{M}_2$</td>
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<td>viscosity (Pa s)</td>
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<td>$\alpha$</td>
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<td>$\mu$</td>
<td>mobility (cm²/s V)</td>
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<td>$\mu'$</td>
<td>real mean value</td>
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<td>conductivity (S/cm or (Ω·cm)⁻¹)</td>
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<td>$\lambda_M$</td>
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<td>$\nu_{\text{mean}}$</td>
<td>mean velocity of gas molecules (m/s)</td>
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<td>$\Delta N_{A,B}$</td>
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<td>$\bar{x}$</td>
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<td>surface energy (N/m)</td>
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<td>total interfacial free energy, s-solid, l-liquid (N/m)</td>
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<td>tensile stress (N/mm²)</td>
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<td>E-modulus (N/mm²)</td>
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<td>$\Theta$</td>
<td>slope at steady state of the $p$ vs. $t$ graph (Pa/s)</td>
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</table>
Literature Part IV


2 R.B. Kaner, R. Anderson, B.R. Mattes, H. Reiss, United States Patent Number 5096586, Table 5

3 R.B. Kaner, R. Anderson, B.R. Mattes, H. Reiss, H. United States Patent Number 5096586, Table 2


7 Kaner, R.B., Anderson, R., Mattes B.R., Reiss, H. United States Patent Number 5096586, Table 3


9 W. A. Neizert, "Thermoformed plastic packaging means", Plast Verarbeiter, 3 (20), (1969) pp. 165-172


20 E. S. Sanders, Ph.D. dissertation, North Carolina State University, Raleigh, NC, 1983.


27 DIN-Norm 66131 "Determination of specific surface area of solids by gas adsorption using the method of Brunauer, Emmett and Teller (BET)"


