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Investigation of new polymeric membranes with controlled architecture for CO₂ capture

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I declare that this is an independent work according to the exam regulations of the Norwegian University of Science and Technology.

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Preface

Membrane separation is considered to be a modern technology, although people used this technology for many years for straining tea or producing fragrances from herbs without realizing its importance. However, the idea of gas separation through membrane is not that simple. Especially, gas separation through the membrane is challenging when the mechanical properties of the membrane, the corrosive environment and the physical and chemical behaviour of gases all interact in different ways. The membrane separation technology for CO₂ capture has got attention mainly for its environmental friendliness and low cost. That is why efficient use of membrane separation can be an attractive solution for CO₂ capture.

This present work has been prepared for those readers who have a basic understanding of carbon dioxide capture and membrane technology. That is why the chapters have been written using existing scientific journals and membrane basics are only a small section in chapter three.

The whole thesis has been divided in two parts and eight chapters. The first part of the thesis gives an overview of different literature study, membrane fundamentals, a few transport mechanisms and theories. The second part shows the experimental part of the thesis mainly describing the results and discussions about the sorption and gas permeation experiment.

Chapter 1 mainly presents the necessity and the present environmental issues concerning about CO₂ emission and its impact on environment. The present carbon capture technology and the membrane separation have been presented in a concise way.

Chapter 2 presents some literature reviews including other's works, discussion and results. **Chapter 3** consists of general membrane definitions, polymeric membrane for gas separation and some important properties of polymers. **Chapter 4** discusses about some transport mechanisms through membranes and theories. **Chapter 5** gives an overview of the characterization methods of gas sorption and permeation. Some features of Magnetic suspension balance (MSB) have been presented here. **Chapter 6** mainly represents the experimental results and the discussion around them.

Chapter 7 gives a conclusion of the whole work. A risk assessment has also been carried out for health and safety reason. This has been included in the appendix.

Abstract

This paper discusses various characteristics of new polymeric membranes for the purpose of CO₂ capture. Different types of single and copolymers were examined; especially by the sorption measurement at different pressures and temperatures. The permeability has been measured for three polymeric membranes and CO₂/N₂ selectivity has been discussed. However, the diffusion coefficient determination by the time lag method and from the solubility and permeability has been compared. For this purpose solubility has been investigated through the sorption experiment by using an MSB (Magnetic Suspension Balance). This paper contains a literature review which describes different studies on membranes and CO₂ capture. The aim of the literature review is to compare and analyze the experimental results reported by different research groups and to identify actual and future development of new membranes for CO₂ capture. The theories, the basic principles of different equipment, give an essential overview to understand the different parts of the thesis. Most of the gas permeation experiments were performed to examine the characteristics of the polymeric membranes at room temperature using N₂ and CO₂ at different pressures. The outcome of the whole project is to observe the characteristics of the polymeric membranes through their diffusion coefficients, solubilities and permeabilities.

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Trondheim, June 16, 2011
Mohammad Mashukur Rahman

Dedicated to all those who are lazy

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List of symbols

Symbol	Description	Units
A	Area	m
Å	Angstrom	10^{-10}
C	Concentration	mol %, $m^3(\text{STP})/m^3$
cP	Centipoise	10^{-3} Pa s
D	Diffusion coefficient	m^2/h , cm^2/s
E	Tensile modulus	Nm^{-2} or Pa
dc/dx	Concentration gradient	mol/m^3m
h	Hour	-
J	Flux	mol/m^2s
L	Membrane thickness	m
M_A	Molecular weight component A	g/mol
M_B	Molecular weight component B	g/mol
p	Pressure	bar
P	Permeability	$cm^3(\text{STP})cm/cm^2barh$
q	Flow rate	$cm^3(\text{STP})/h$
Q	Permeance	$m^3(\text{STP})/m^2barh$
s	Seconds	-
S	Solubility	$m^3(\text{STP})/m^3bar$
T	Temperature	$^{\circ}C$, K
T_b	Boilin point	$^{\circ}C$, K
T_g	Glass transition temperature	$^{\circ}C$, K
X	Driving force	-
x	Molar fraction	-

Greek letters	Description	Units
α	Membrane (perm)selectivity	-
\square	Henry's law constant	
μm	Micrometer	10^{-6}
Δ	Delta	-
Abbreviations	Description	Units
PEG	Poly ethyleneglycol	-
PSD	Pore size distribution	-
PSf	Polysulfone	-
PVAm	Polyvinylamine	
PVP	Polyvinylpyrrolidone	-
PDMS	poly(dimethyl siloxane)	
PEBAX [®]	polyether-block-amide	

Conversion

Barrer	$=10^{-10}\text{cm}^3(\text{STP})\text{cm}/\text{cm}^2\text{s cm Hg}$ $=27.4 \times 10^{-10}\text{m}^3(\text{STP})\text{m}/\text{m}^2\text{h bar}$
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Chapter 1 Introduction

1.1 Background

CO₂ releases due to the dependence on fossil fuels are resulting in climate change which is now an important environmental issue. According to IPCC (Intergovernmental Panel on Climate Change: 2007) the emission of CO₂ to the atmosphere by the use of fossil fuels increases 3×10^{12} kg/year. CO₂ is a greenhouse gas and causes an increase in temperature on earth. Global temperature data are available from about 1860 to the present. Variation of earth surface temperature from 1860 to 2000 has been shown in the figure 1.1 [1]:

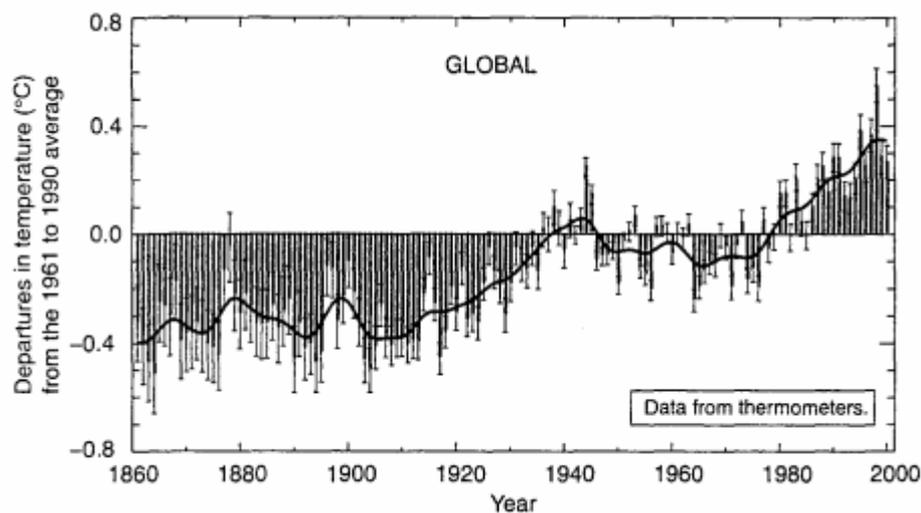


Figure 1.1.1: Variation of earth's surface temperature over the period 1860 to 2000 (IPCC 2001) [2]

The main problem which should be taken into account is that a large amount of CO₂ almost 98% on earth gets dissolved in the oceans which is 4.1×10^{16} kg. As the solubility of CO₂ decreases with increasing temperature of the ocean by 3% per degree Kelvin, the equilibrium between the atmosphere and the ocean shift towards the atmosphere and increases the solubility of CO₂ to the atmosphere (7.5×10^{14} kg at the moment) [1]. The result is more greenhouse gas emission to the atmosphere which affects the natural habitat of the world and in particular, global warming. That is why modern technologies are based on eco friendly ideas as the climate becomes more sensitive. As the economy is greatly dependent on fossil fuels, the production of CO₂ is inevitable. This requires technologies to capture CO₂ in an efficient way. That is

why, Carbon dioxide capture and storage becomes familiar and of course as a modern technology.

Carbon dioxide capture and storage (CCS) is a process to mitigate CO₂ emission to the atmosphere by separating CO₂ from industrial and energy related sources before it releases to the environment and storing it underground in an isolated geological formation for a long time. CCS gets popularity for its flexibility in reducing CO₂ emissions and reduced mitigation cost [3].

CCS process primarily based on three types; namely: post-combustion, pre-combustion and oxyfuel combustion. Several factors like concentration of CO₂ in the gas stream, pressure and the type of fuel determine which process should be selected [3]. A schematic representation of CCS systems has been shown below:

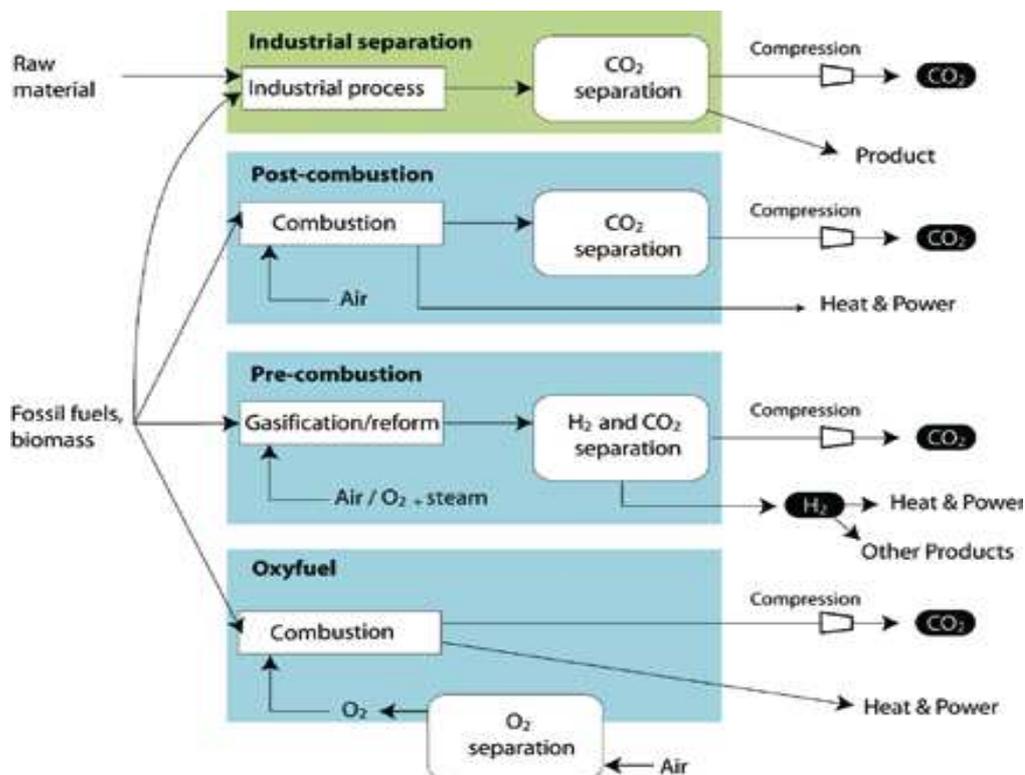


Figure 1.1.2: Schematic representation of capture systems. Fuels and products are indicated for oxyfuel combustion, pre-combustion (including hydrogen and fertilizer production), post-combustion and industrial sources of CO₂ (including natural gas processing facilities and steel and cement production) (from CO₂CRC) [3].

According to IPCC (Intergovernmental Panel on Climate Change): “The net reduction of the CO₂ through CCS depends on the fraction of CO₂ captured, the increased CO₂ production resulting from loss in overall efficiency of power plants or

industrial processes due to the additional energy required for the capture, transport and storage and the fraction of CO₂ retained in storage over the long term” [3]. The energy requirement for a power plant with CCS is almost 10-40% more than a same capacity plant without CCS system. However, the present CCS technology reduces 85-95% of CO₂ emissions to the atmosphere in a process plant [3].

In a typical power generation plant where CO₂ is the final product of the oxidative reactions and so, its presence is unavoidable. Therefore, gas separation becomes challenging for CO₂ emission reduction. At present four fundamental technologies have been used or being developed are- adsorption, absorption, cryogenic separation and membrane separation [4].

The membrane separation is relatively modern technology and started in 1980's when techniques were developed for hydrogen separation, particularly hydrotreaters in refineries, for O₂/N₂ separation, for CO₂ separation from process natural gas [4]. The development of copolymers opens a wide and large scale use of membranes in industries where a thin selective layer of copolymer is attached with a non selective and inexpensive support. At present, the carbon capture membrane can be used for separating CO₂ from post combustion flue gas. Different kind of techniques and advanced materials are being used to develop better separation techniques through research and investigation [4].

1.2 Aim of the thesis

The main objective of this paper is to study different literatures on membrane and investigate how other researchers have done their work especially on gas sorption and permeation for CO₂ separation. Their results, comments and experimental procedures can give a useful idea about the scope and constraints of the whole thesis. However, this thesis is limited to pure gas sorption measurement and permeation especially to CO₂ and N₂ (light gas). The gas permeation test basically has done for the purpose of commenting on diffusion coefficient. The whole project shows the necessity and importance of finding a solution for CO₂ capture by membrane separation to contribute to pollution free environment.

Chapter 2 Literature review

2.1 Polymeric membrane material selection guideline

Polymeric membrane materials optimization has become very popular in the research field as there are lots of possibilities to get better separation performance. Basically, the selectivity, permeability and diffusivity of the polymer can give a very good guideline about the choice of gas separation techniques. For, example, CO₂ shows higher solubility in polymers than light gases as it has a higher condensability (typically determined by critical temperature) than them. In the same way, on the basis of relative molecular size difference CO₂ has higher diffusivity than CH₄ and almost similar like N₂ and lower than H₂. That is why, for CO₂/CH₄ separation the choice of membrane materials should be high diffusivity selective by preparing rigid polymers with high glass transition temperature. The permeability of CO₂ is ensured by increasing the fractional free volume.

However, the materials for CO₂/light gas separation suggest that solubility selectivity could be a better choice. In fact, for CO₂/H₂ separation, this solubility selectivity is required for the unfavourable diffusivity of H₂. If the penetrant size difference is not large, as in the case of CO₂/N₂; solubility selectivity can be a good choice of separation [5].

If permeability can be written as:

$$P = D \times S \quad (2.1.1)$$

Where, D and S are the average effective diffusivity and apparent penetrant solubility respectively. Then for two gases a and b, the ratio of the permeabilities which is basically describes the selectivity is:

$$\alpha_{a/b} = P_a / P_b = (D_a / D_b)(S_a / S_b) \quad (2.1.2)$$

D_a / D_b is the diffusivity selectivity and S_a / S_b represents solubility selectivity.

Thus, controlling these two selectivities, the polymer can be made suitable for specific gas separation scheme. The diffusivity greatly depends on the molecular size, fractional free volume, chain flexibility and polymer-penetrant interaction [5].

Lin and Freeman [5] in their journal represent these separation guidelines which suggest that the solubility has a correlation with the polymer matrix. For this purpose,

they mentioned the Flory-Huggins theory to explain that, gas solubility not only depends on gas physical properties but also on the interaction with polymer matrix. However, their assumption is based on ideal situation. Considering polymers like liquid solvent Lin and Freeman have shown some model equations and they have presented some graphs and data which show the relation of solubility parameter and solubility of CO₂/N₂ system. Lin and Freeman [5] wanted to investigate the highest solubility of CO₂ in polymers containing different type and amount of polar groups. Their investigation concludes that CO₂ interaction with polymer is a prospective field for polymeric membrane research on CO₂/light gas separation. However, the information about such interaction is not adequate. That is why more investigation of various polar groups or copolymers is required [5].

2.2 Large scale gas separation strategies

Most of the literatures written on the gas separation by polymer membranes mention the diffusivity and solubility selectivity. However, the two big challenges for gas separation is to find the higher permselective membrane for a definite application and to make the membrane capable of withstanding in aggressive and complex feed. Koros and Mahajan [6] from the department of Chemical Engineering, The University of Texas at Austin, has discussed these two challenges by comparing different membranes and their transport mechanism. However, their discussion is limited to the solution diffusion mechanism, facilitated transport and ion-conducting membranes. The interesting part of their discussion is the presentation of the current application of the membranes and transport mechanisms as well as to find the scope for optimization of the membrane applications. Koros and Mahajan [6] has discussed the importance of cross-linking of polymers to overcome one of the big challenges namely- retaining the membrane properties. In this purpose they illustrate monomers and cross- linked polymers reaction scheme. However, the most attractive part of their discussion is the choice of strategies for different application of membranes in different situations with the existing membrane technologies. For example, the mixed matrix approach for air separation or mixed matrix along with cross-linking or CMS (carbon molecular sieves) for hydrogen recovery, natural gas sweetening are good choices for economic consideration. However, the discussion mainly shows some possibilities and opportunities than applying effectively in real situation. Koros and Mahajan [6]

conclude their discussion by highlighting the technical barriers for the implementation of these opportunities [6].

2.3 Combination of poly(ethylene glycol) and poly(dimethyl siloxane) for efficient CO₂ separation

For the technical barrier the separation of CO₂/light gas in large industrial application is not yet satisfactory. Reijerkerk et al. [7] have presented some experimental results on PDMS-PEG [poly (dimethyl siloxane) - poly (ethylene glycol)] graft polymer and PEBAX[®] which is a polyether-block-amide and they have shown that the gas selectivity has been achieved by solubility selectivity. As these polymers have low glass transition temperature they have an advantage of high CO₂ diffusivity as well as solubility into the matrix. Different physical properties like density, gas permeability and pure gas sorption have been measured at room temperature. Mostly the gas permeation properties have been measured at 4 bar and a temperature of 35⁰C. Their results show how the permeability of CO₂ increases with increasing additive mass fraction. Especially, the CO₂ permeability increases from 100 Barrer [1 Barrer=10⁻¹⁰cm³(STP) cm/cm²s cm Hg] for PEBAX[®]1657 to 532 Barrer with 50 wt% PDMS-PEG [poly(dimethyl siloxane)- poly(ethylene glycol)] additive, while only PEG₂₀₀ increases 172 Barrer [7]. This trend is shown in figure 2.3.1.

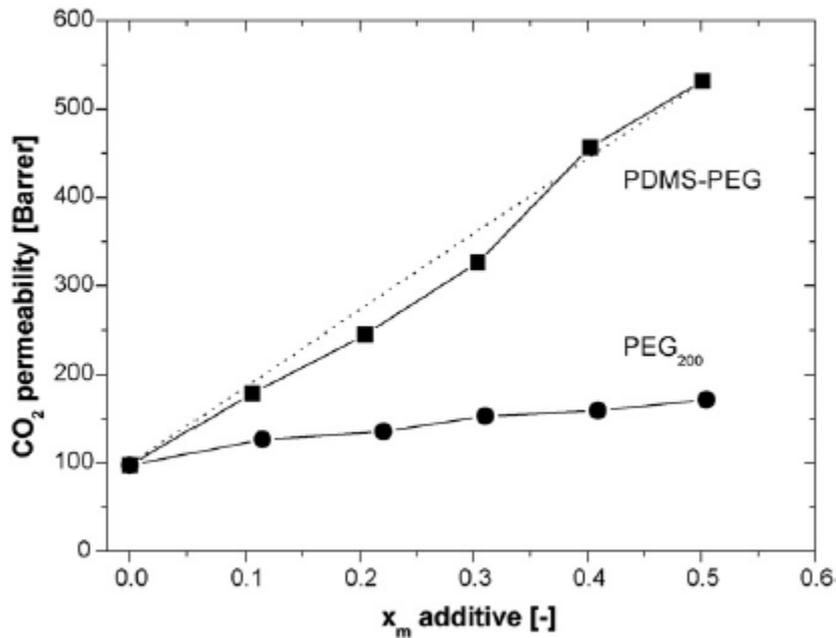


Figure 2.3.1: Pure gas CO₂ permeability at 35⁰C and 4 bar as a function of additive mass fraction of blend membranes with (i) PDMS-PEG (ii) PEG₂₀₀ [7].

The dashed line in this graphical representation is the theoretical PDMS influence to CO₂ in the same blend polymers using the data from Merkel et al. [8] as well as Singh et al.[9]. Actually they have used the parallel model equation which can be written as:

$$P_b = \phi_1 P_1 + \phi_2 P_2 \quad (2.3.1)$$

Where, P_b is the permeability of the blend, P_1 and P_2 are the permeabilities of component 1 and 2 respectively and ϕ_1 and ϕ_2 are the volume fraction of the component 1 and 2. Thus, the theoretical contribution of PDMS [poly(dimethyl siloxane)] for CO₂ permeation can be theoretically described.

In the case of non-polar gases their [7] investigation shows the same trend for the additive fraction added. As this specialization project report is primarily focused on CO₂, the data and experimental results of Reijerkerk et al. [7] have been shown only for CO₂. However, they have investigated other gases. Figure 2.3.2 shows CO₂/ light gas selectivity.

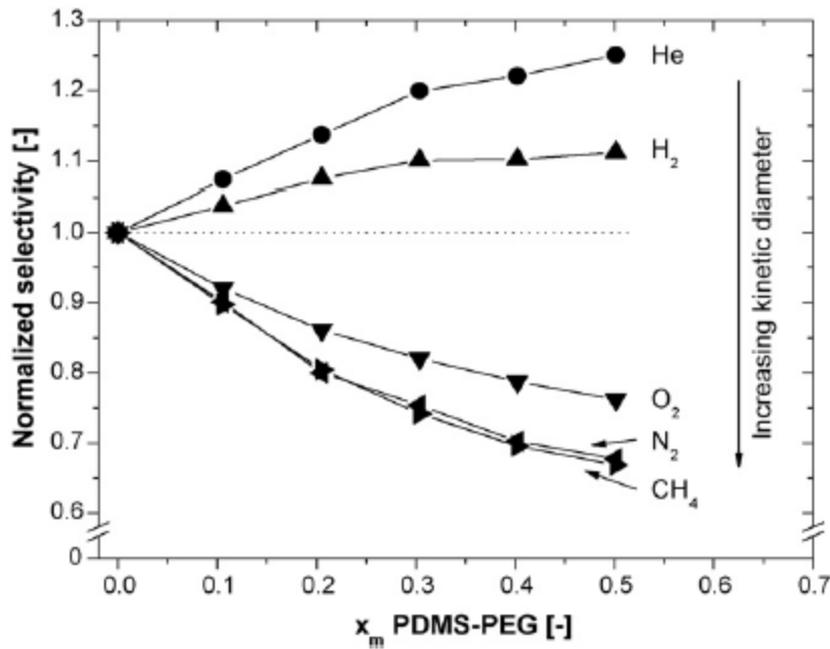


Figure 2.3.2: Normalized pure CO₂/light gas selectivities at 35⁰ C and 4 bar as a function of additive mass fraction of blend membranes with PDMS-PEG [7].

They infer for this trend is that the free volume of the polymer matrix has been increased for the additives. They also have studied CO₂ sorption behaviour. Only a few investigation results have been shown in figure 2.3.3 and 2.3.4 as an example of their work [7].

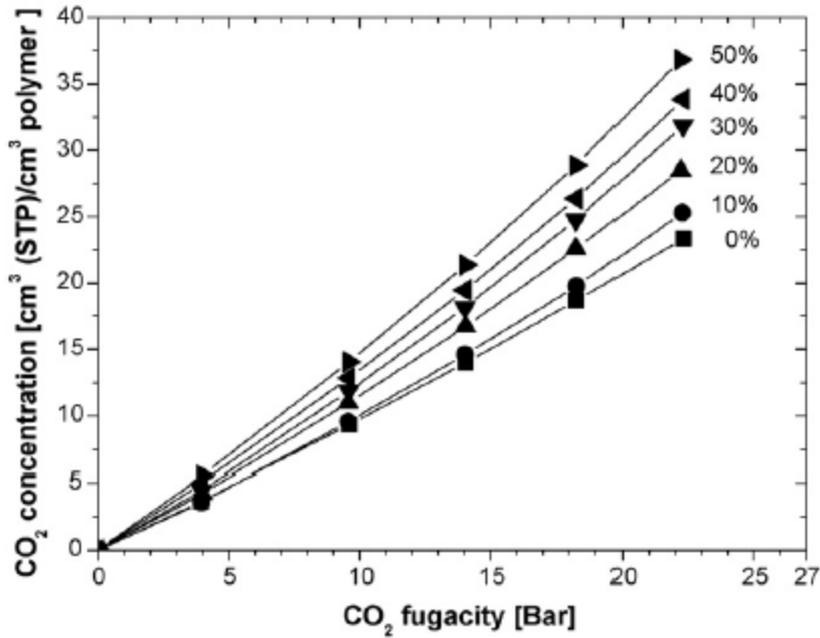


Figure 2.3.3: CO₂ concentration (cm³ (STP)/cm³ polymer) as a function of CO₂ fugacity at 35⁰C for PABX[®] 1657/PDMS-PEG blend membranes with different PDMS-PEG additive blend ratio [7].

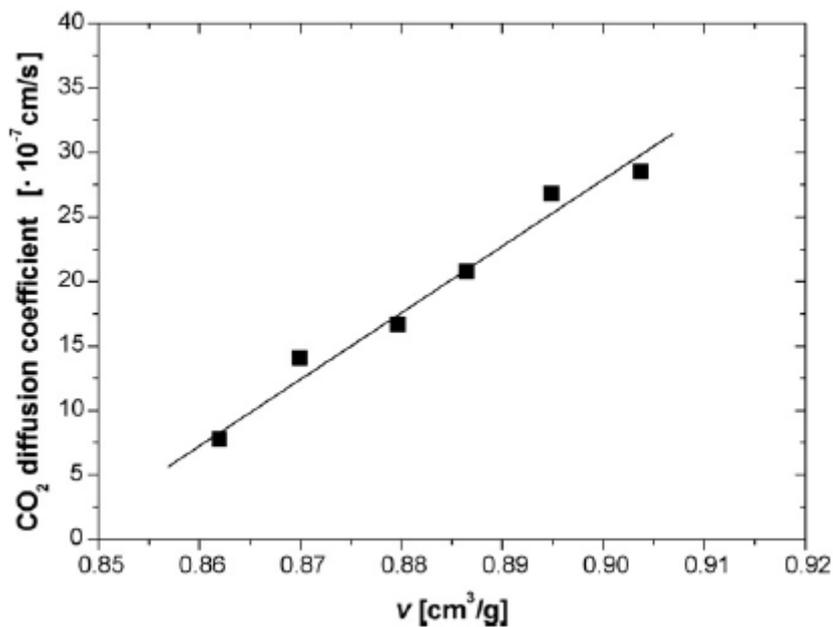


Figure 2.3.4: Diffusion coefficient of CO₂ at 35⁰C as a function of the polymer specific volume for PABX[®] 1657/PDMS-PEG blend membranes [7].

Using the solution diffusion model the diffusion coefficient has been calculated from the permeability and solubility measurement where a higher specific volume points at the higher concentration of PDMS-PEG in the blend.

Actually, Reijerkerk et al. [7] have investigated many other aspects like the competition effect of plasticization and hydrostatic pressure and their influence on permeabilities. Their work summarizes that higher permeability together with good selectivity can be achieved with a proper choice of blending and copolymer.

2.4 Novel fixed-site-carrier (FSC) Polyvinylamine membrane for carbon dioxide capture

As higher permeability lowers the selectivity, so the approach to get both of them high is to use a carrier. Kim et al. [8] describe the carrier mediated diffusion in fixed-site-carrier Polyvinylamine (PVAm) membrane. The fixed site carrier on polymer backbone in presence of water will go for a reversible reaction with CO₂ and transport it by the so called facilitated transport while the light gases like methane or nitrogen will penetrate the membrane with only solution diffusion mechanism [17].

Kim et al. showed the role of the fluoride ion in facilitated transport. At the same time they indicated the difference of transport of CO₂ with humidity and without it. The basic difference in dry and wet case is that in dry membrane the acid base interaction between CO₂ and amine occurs, in contrast, CO₂ does not interact with amino groups in presence of humidity rather amino group act as a catalyst for CO₂ hydration. The CO₂ basically transported as HCO₃⁻. Again, the light gases like CH₄, N₂ and O₂ will be hindered for the low solubility and non polar nature of these gases. So a better selectivity can be achieved. [17]

So, the facilitated transport is a combination of both surface diffusion and the reversible reaction. However, they assumed the diffusion is rate limiting and the sum of the carrier mediated diffusion and the Fickian diffusion will be the total flux of the permeate [17].

Hence the total flux of the CO₂ through the membrane,

$$J_A = \frac{D_A}{l}(C_{A,0} - C_{A,l}) + \frac{D_{Ac}}{l}(C_{Ac,0} - C_{Ac,l}) \quad (2.4.1)$$

Where, D_A and D_{AC} are Fickian and carrier mediated diffusion respectively. C is the concentration of the component A and its complex AC. The thickness of the membrane is l.

However, the diffusion is not rate limiting solely. The reversible chemical reaction is rate limiting for a short interval. The most interesting feature of their work is, it has got the highest selectivity than some other published work [17]. The selectivity of the reviewed Polyvinylamine (PVAm) membrane has been shown in table 2.4.1.

Table 2.4.1: Some features of Polyvinylamine (PVAm) facilitated transport membranes [17]

Membrane	Selectivity	Flux ^a	System	ΔP_{CO_2} ^b (bar)
Polymerized membrane from diisopropylamine	17	1.2	CO ₂ /CH ₄ 3.5 vol % CO ₂	—
Poly {2-(N,N-dimethyl) aminoethylmethacrylate}	130	2.7×10^{-3} -2.7×10^{-2}	CO ₂ /N ₂ 2.7–58 vol % CO ₂	0.05
Polyethylenimine/poly(vinyl-alcohol)	230	2.7×10^{-3}	CO ₂ /N ₂ 5.8–34.4 vol % CO ₂	0.07
Membrane from polyvinylpyrrolidone by hydrolysis	48.1 39.3	4.6×10^{-1} 1.2×10^{-1}	CO ₂ /CH ₄ 50 vol % CO ₂	0.02 0.07
Membrane from polyvinylpyrrolidone by hydrolysis	212.1 155.9	2.1 4.4×10^{-1}	Pure CO ₂ and CH ₄	0.01 0.07
Polyvinylamine on polysulfone support	700–1100	8.4×10^{-3} -1.0×10^{-2}	Pure CO ₂ and CH ₄	2–4

^a The units of flux and pressure are converted to units used in the current paper (m³ (STP)/m² bar hr).

^b ΔP represents the approximate partial pressure difference over the membrane (feed-permeate side).

Chapter 3 Membrane Concept

3.1 Membrane definition and classification

A membrane performs as a selective barrier, separating one particular component from a mixture of components of a feed stream. In a membrane module the permeate passes through the membrane leaving the retentate (feed stream minus the permeate) on the feed side. The retentate may either exit the membrane module after separating the permeate (cross flow) or be continuously build-up on membrane (dead-end flow) [4]. Two most common membrane configurations have been represented below in figure 3.1.1.

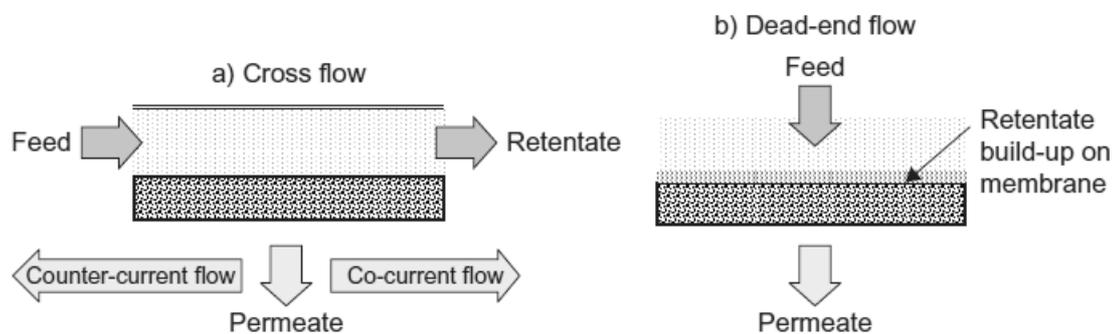


Figure 3.1.1: Cross flow (a) and dead flow (b) membrane configurations [4]

The separation process depends on application, different types of membranes employed, process parameters and type of module [4].

Membranes can be classified according to porosity namely-porous and non porous or dense membrane. Porosity greatly influences the gas transport mechanism through membranes. For porous membrane viscous capillary flow, Knudsen diffusion, molecular sieving, surface diffusion and capillary condensation are the main transport processes which are dependent on pore diameter and mean free path of the gas molecules. However, for nonporous membranes solution-diffusion, facilitated transport, ion-exchange is the transport mechanism governing the separation [4].

3.2 Membrane types and their characteristics

Membrane types are determined by their preparation method and materials used. The polymeric, ceramic or metallic membrane can be produced in either symmetric (isotropic) or asymmetric (anisotropic) structure by the preparation method [4]. A schematic representation of the different type membrane structures is shown in figure 4.

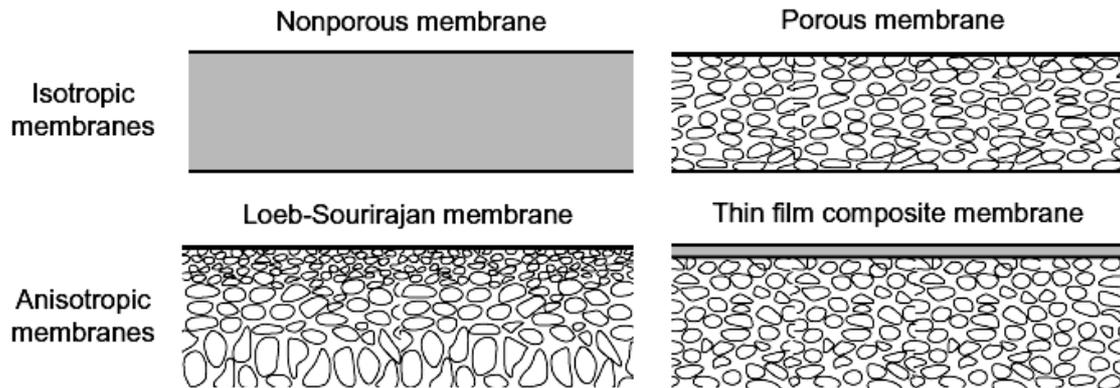


Figure 3.2.1: Different types of membranes on the basis of their physical structure [4].

However, asymmetric (anisotropic) structure with a thinner selective layer on a thicker nonselective support is an attractive choice for high flux rate. For example, Zeolite asymmetric membranes are prepared by the thin synthetic zeolite layers on alumina or porous stainless steel tubes or disks. On the basis of this physical structure, membranes can be characterized as shown in table 1 [4].

Table 3.2.1: Characteristics of membranes according to their physical structure [4]

Structure	Characteristics
Symmetric (isotropic) membranes	Porous or non porous membranes with a homogenous structure all over the membrane thickness
Asymmetric (anisotropic) membranes	A thin layer of porous or nonporous membranes supported on a composite
Liquid membranes	Especially a liquid selective phase bonded or immobilized within the polymeric or ceramic pore space.

3.3 Polymeric membrane for gas separation

Polymeric membranes are widely used for CO₂ removal from natural gas since 1980's. Mostly, spiral wound membrane module or hollow fiber membrane module are suitable for asymmetric polymeric membranes based on cellulose acetate. However, pretreatment of the feed gas is a prerequisite for separation due to the heavy hydrocarbon contamination or fouling of the membrane modules [4].

One major disadvantage of polymeric membrane is that they are sensitive to organic solvent as they swell or dissolve. However, it is possible to fit them in proper operating conditions by modifying their physical and chemical properties.

3.3.1 Polymer characteristics

The physical and chemical properties of the polymers can be explained by the following factors [10]:

- Physical behaviour
 - Intermolecular force between functional groups of the polymer chain
 - Size of the functional groups
 - Polymeric chain flexibility
- Chemical phenomena in different environment
 - Bond energy
 - Ionic nature of the bond

The physical behaviour mainly determines the surface properties of the polymer while the chemical properties are also important in the same manner. The fact is, if the solubility of a polymer in a solvent is satisfactory but the structural integrity cannot be retained it is basically useless. For example, silicon polymers membranes are more suitable for high temperature applications than aliphatic hydrocarbon polymers because their bond dissociation energy of the siloxane bond (Si-O) is higher compared to C-C bond. In contrast, fluorocarbons like Teflon are suitable for alkaline environment as siloxane bond is prone to hydrolysis due to its ionic nature (50%). Some other factors should be noted that poly(dimethylsiloxane) or PDMS films exhibits irregular cross section (large at substituted silicon atom and small at oxygen atom) while poly(tetrafluoroethylene) or PTFE is more regular. Besides these three

physical behaviours, there are other factors that may influence polymer characteristics. However, one important parameter that is related to these three physical behaviours or several more factors is glass transition temperature, T_g [10]. Glass transition temperature T_g of a polymer indicates the degree of crystallinity that is, the temperature at which the cooling rate of a polymer exceeds that of crystallization [11].

3.3.2 Polymer structure and glass transition temperature, T_g

Generally, high glass transition temperature indicates the rigidity of the polymer and high stability in solvents. However, the chain mobility of a polymer is greatly influenced by increasing temperature in the glassy state as the segments rotation is restricted in this state. At the glass transition temperature the rotation becomes freer and the chain flexibility and interaction are the two important parameters which determine this glass transition temperature. Most physical properties like specific volume, specific heat, permeability change at this temperature as the polymer moves from glassy to rubbery state. Another important physical property which is linked to the glass transition temperature is fractional free volume which is virtually constant below T_g . Above T_g the free volume increases linearly with temperature. The relation among temperature, specific volume and free volume is shown in figure 3.4.1 [12].

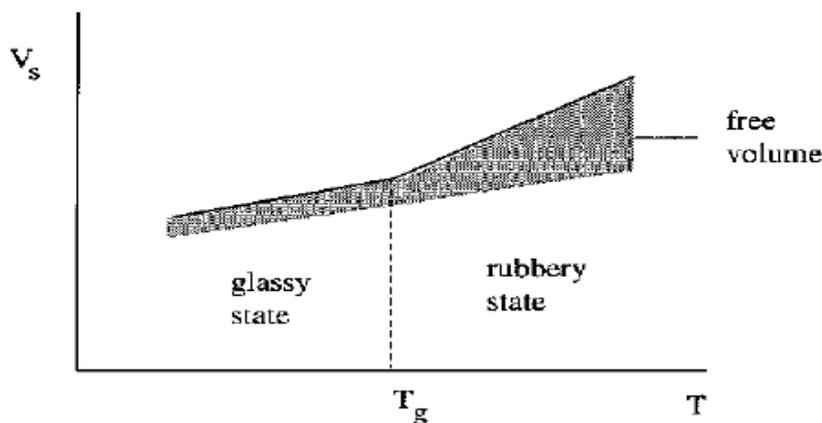


Figure 3.3.2: specific volume and free volume as a function of temperature [12]

For many hard structure polymers, the glass transition temperature is at room temperature or higher (Polystyrene, polymethyl methacrylate, polycarbonate etc.) while easy crystallizable polymers (polyethylene, polypropylene, polyethylene

terephthalate) show the opposite trend [6]. The crystallinity of a polymer affects the mechanical properties as well as the transport properties of the polymer. The influence of the crystallinity on the tensile modulus has been shown in figure 3.4.2 [12].

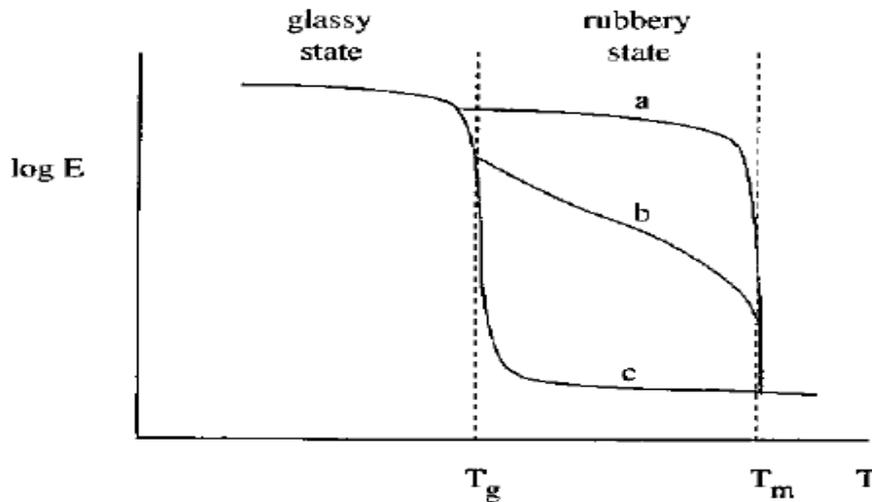


Figure 3.3.3: Tensile modulus of i) crystalline ii) semi crystalline iii) amorphous polymer as a function of the temperature [12].

Elastomers which have low T_g are more permeable than the glassy polymers with high T_g [12]. However, this is not all the time valid. For example, polyphenylene oxide has a high T_g value as well as permeability towards nitrogen and oxygen.

3.3.3 Selectivity and permeability of gases in rubbery and glassy polymers

The separation capacity of a membrane for gases can be best described by the selectivity which is the ratio of the gas permeability. For example, if two gases a and b have permeability P_a and P_b respectively; then, the selectivity,

$$\alpha_{a/b} = P_a / P_b = (D_a / D_b)(S_a / S_b) \quad (3.4.1)$$

The ratio D_a / D_b is the diffusivity ratio of the two gases known as mobility selectivity based on the size of the gas molecules. On the other hand, S_a / S_b is the sorption coefficients ratio or solubility selectivity which indicates the difference in solubility of the two gases in the polymer membrane. The mobility selectivity, D_a / D_b shows that the permeation of small gas molecules is higher than for larger molecules as the diffusion coefficient decreases with increasing molecular size. Whereas, sorption or

solubility coefficient is dependent on the energy requirement of the gas to be sorbed into the polymer, which decreases with increasing gas condensability. It is clear that the sorption selectivity actually increases with increasing molecular size as large molecules condense easily than small molecules. Hence, the sorption or solubility selectivity and mobility selectivity are quite different for different molecular size. That is why, the parallel effect of solubility selectivity and mobility selectivity determines which one will be dominant for a pair of gases and a single polymeric membrane. The most significant feature is that, these two selectivity (solubility and mobility) acts different in the two types of polymers – glassy and rubbery [13].

The glassy polymers are rigid and this physical property determines their mode of selectivity will be mobility or diffusion based. So, the small gas molecules are likely to be transported faster. For example, for separating organic vapour from nitrogen through polyetherimide (glassy polymer), nitrogen is permeate faster [13].

In contrast, for the same gas mixture of nitrogen and organic vapor, if a polyisoprene rubbery polymer is used then the organic vapour permeate faster due to its larger molecules. This means the solubility selectivity is dominant here [13].

A graphical representation of the permeability as a function of gas molar volume for a rubbery and glassy polymer is shown in figure 10 [13].

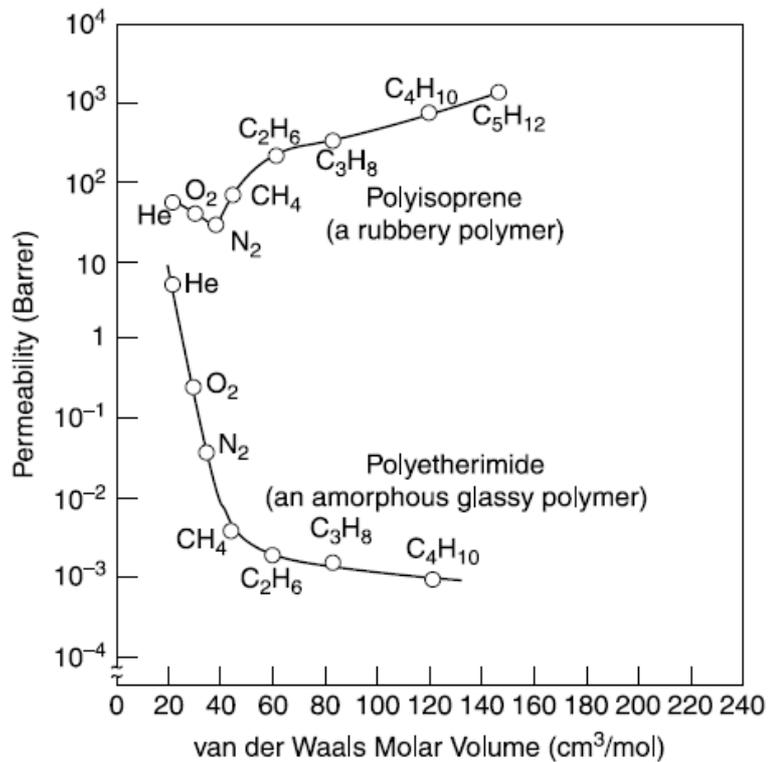


Figure 3.4.1: Permeability of a rubbery and a glassy polymer as a function of molar volume [13].

Rubbery polymers are more permeable than glassy polymers as the permeability of oxygen in polyisoprene is 100 times more than in polyetherimide which is shown in figure 10. The higher permeance has important advantage in the design of the membrane module as the higher permeability allows less area of the membrane and hence less cost effective operation [13].

Chapter 4 Transport mechanisms and theories

4.1 Solution diffusion transport mechanism

This process of gas separation is mainly governed by two steps. First step is initiated by dissolving the gas into the membrane and the next step is the diffusion through the membrane. That is why it is called solution diffusion transport process. For example, Hydrogen when passes through a dense polymeric membrane it adsorbed first on to the membrane surface where it dissociates and then the protons diffuse through the membrane lattice and combine on the permeate side followed by a desorption from the membrane surface [4]. A simple representation of solution diffusion transport process has been shown in figure 4.1.1 [4].

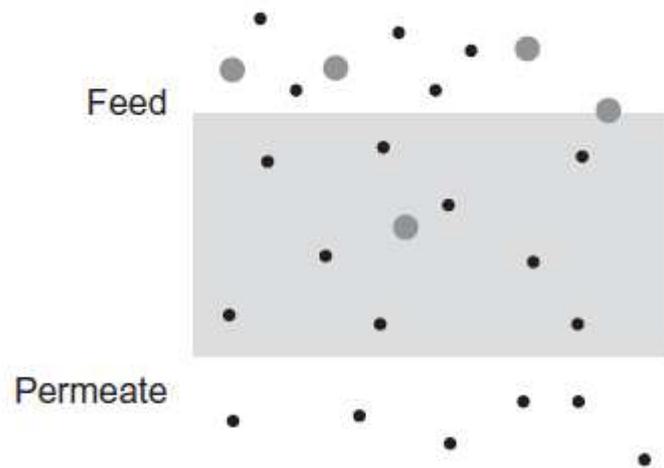


Figure 4.1.1: Solution diffusion transport mechanism [4]

The speed of the solution diffusion process determines the membrane's effectiveness; that is, how quickly CO_2 or H_2 adsorbed and diffuse through it [4].

According to Henry's law, the amount of gas which is dissolved in unit volume of a medium is proportional to the partial pressure of the gas in equilibrium with the medium at a given temperature [4]. That is, $C = P/\square = P K$ (4.1.1)

Where, C = dissolved concentration

P = partial pressure of the gas in equilibrium

\square = Henry's law constant

K = the solubility of the component gas.

In the case of CO_2 diffusion through a dense membrane by Fick's first law, this can be stated as:

$$J_{CO_2} = D_{CO_2} \Delta C_{CO_2} / L \quad (4.1.2)$$

Where, J_{CO_2} = flux through unit area of the membrane (mol/m^2sec)

D_{CO_2} = Diffusivity of CO_2 through the membrane (m^2/sec)

L = membrane thickness (m)

ΔC_{CO_2} = concentration difference across the membrane ($m^3 (STP)/m^3$)

Now combining Fick's law and Henry's law:

$$J_{CO_2} = K_{CO_2} D_{CO_2} \Delta P_{CO_2} / L \quad (4.1.3)$$

Where, K_{CO_2} and ΔP_{CO_2} are the solubility of CO_2 and partial pressure difference across the membrane respectively [4].

The above equation (4.1.2) clearly shows the permeability of the membrane is the product of the diffusivity and the solubility of CO_2 into the membrane. For two component gases the ratio of the fluxes (that means their permeances) will be the selectivity [4].

The solution diffusion mechanism can be observed in polymeric dense membranes. However, the maximum flux through the membrane and the cost greatly depend on the thickness of the membrane. That's why a careful and special preparation of the membrane is very important. As already has mentioned that the permeability is the product of the solubility and the diffusivity. So, to control the permeability, the

solubility can be altered by changing the chemical composition of the polymer while the diffusivity is greatly affected by the physical packing of the polymer [4].

The temperature plays an important role as it will determine the type of the polymer to be used in the process. In particular, the polymers which are used above glass transition temperature T_g are rubbery while the polymers used below T_g are glassy. Rubbery polymers are flexible and usually have higher permeability than selectivity. The selectivity of the polymers may drop sharply with increasing temperature which limits the application of the polymer for not having better separation. So, one important approach to solve the problem of selectivity drop may be the use of a copolymer or hybrid (polymer + inorganic) membranes [4].

4.2 Dual sorption theory

As for the solution diffusion mechanism, the adsorption of the gas molecules onto the polymeric membrane is important. So imperfect packing can help improve the solubility (as there is always microscopic free volume between the polymer chains) due to adsorption of gas molecules onto the void space [4]. This adsorption can be represented by Langmuir's adsorption equation:

$$C_{ads} = C_{max} a P / (1 + a P) \quad (4.2.1)$$

Where, C_{ads} = adsorbed concentration on the void space (m^3 (STP)/ m^3)

C_{max} = maximum adsorbed concentration (m^3 (STP)/ m^3)

a = Langmuir adsorption constant

P = partial pressure of the component gas (bar)

So the total bulk concentration is the sum of the dissolved concentration of the gas by Henry's law and the adsorbed concentration in the micro voids according to Langmuir's adsorption; which together give the dual sorption model and can be written from equation (1) and (3) as:

$$C_i = P K + C_{max} a P / (1 + a P) \quad (4.2.2)$$

However, the dual sorption model can be better suited below glass transition temperature T_g and for the glassy state [4]. The graphical representation of dual sorption model has been shown in figure 4.2.1.

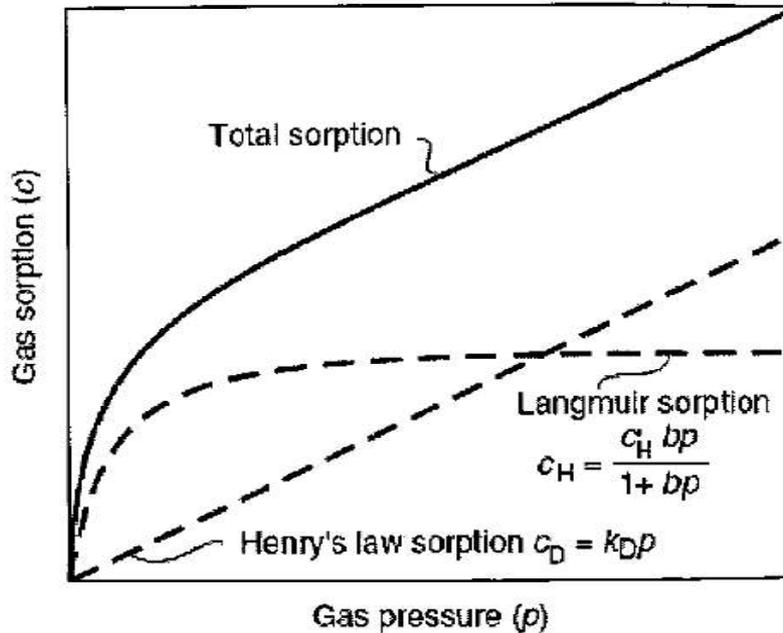


Figure 4.2.1: Dual sorption model [14]

4.3 Flory-Huggins theory: gas solubility correlation with structure

The interaction of the penetrant with a rubbery polymer can be formulated by Flory-Huggins theory:

$$\ln a_i = \ln \phi_2 + (1 - V_i / V_p)(1 - \phi_2) + \chi(1 - \phi_2)^2 \quad (4.3.1)$$

where, χ = interaction parameter. According to the theory, when $\chi > 2$ the interaction between the penetrant and the polymer is thought to be small. However, a value $0.5 < \chi < 2$ shows a strong interaction between the penetrant and the polymer matrix and also high permeabilities [5].

a_i is the penetrant solubility or activity.

V_i = partial molar volume of the penetrant.

V_p = Partial molar volume of the polymer.

ϕ_2 = volume fraction of the gas dissolved in the polymer matrix.

$$\phi_2 \text{ can be written as, } \phi_2 = \frac{(C / 22414)V_p}{1 + (C / 22414)V_p} \quad (4.3.2)$$

where C is the penetrant concentration in the polymer. If the sorbed gas concentration is very low that is $\phi_2 \ll 1$ and the penetrant activity, a_i can be described as P/P_{sat} for ideal situation (where P_{sat} is the penetrant saturation vapor pressure at given temperature), then equation (4.3.1) and (4.3.2) give Henry's law. It can be written as, $C = k_D P$ where k_D is the infinite dilution solubility coefficient [5].

$$k_D = \frac{22414}{P_{\text{sat}} V_p} e^{-(1+\chi - V_p/V_i)} \quad (4.3.3)$$

Thus Flory-Huggins theory shows that the gas solubility in the rubbery state depends not only saturation vapour pressure and partial molar volume but also on its interaction with the polymer matrix. So a positive interaction (decreasing χ) can ensure an exponential increase in penetrant solubility which is shown in equation (4.3.3) [5].

4.4 Facilitated transport membranes

Facilitated transport mechanism has been evolved to enhance the gas transport through membrane by increasing flux rate using a carrier which is attached with the membrane. In fact, solution diffusion mechanism is relatively slow and a passive transport system which is limited by low permeate flux rate for low solubility and diffusivity. One advantage of carrier mediated transport is that, it can pass a gas molecule across the membrane even from a region of low concentration to high concentration. Carrier can be fixed or mobile to which the gas molecules react and form complexes. The complex is mainly a reversible reaction product. The complex can diffuse through the membrane and by the reversible reaction it can liberate the permeate in the downstream of the membrane. This has been illustrated in figure 4.4.1 where CO_2 is passing through the cellulose acetate membrane by facilitated transport mechanism [4].

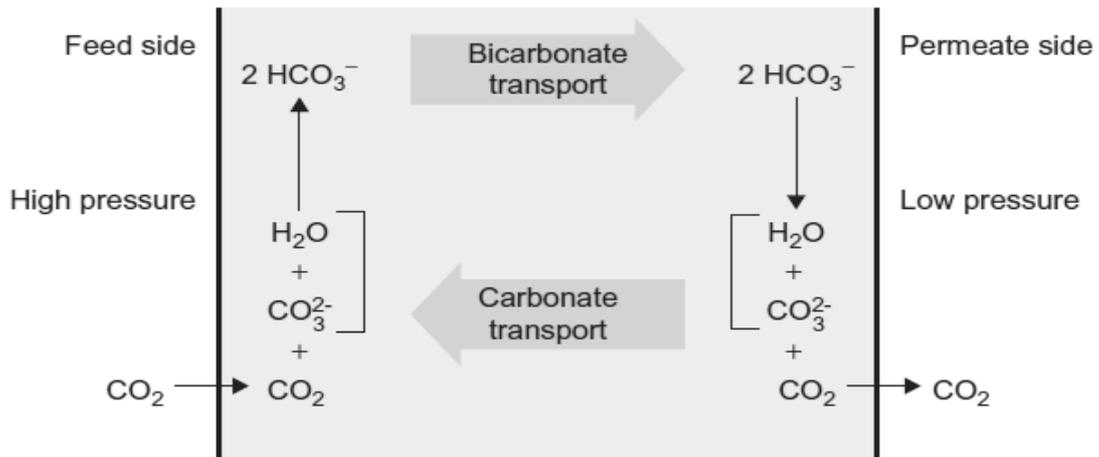
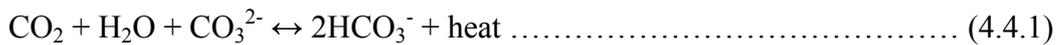


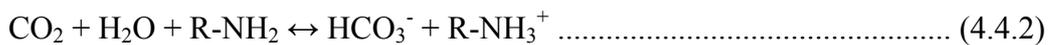
Figure 4.4.1: Facilitated transport of CO₂ in supported liquid membrane (mobile carrier-carbonate) [4]

The aqueous solution of carbonate acts as a mobile carrier for CO₂ by initiating the following reaction:



The reverse reaction occurs at the permeate side while the CO₂ is liberated.

In the same manner CO₂ can be transported by a fixed site carrier like amine groups. The CO₂ which diffuses through membrane reacts with water and amine groups and subsequently forms bicarbonate. Again, the CO₂ releases at the permeate side by the reversible reaction [4]:



This has been shown in figure 4.4.2.

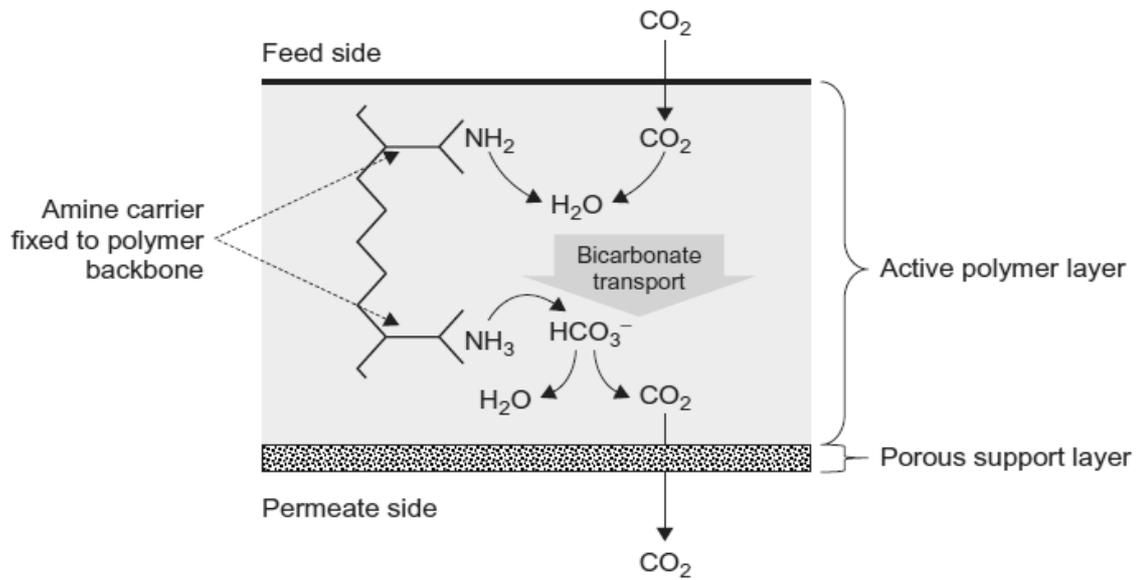


Figure 4.4.2: Facilitated transport of CO₂ through membrane (fixed carrier – amine groups) [19]

For amine facilitated transport, secondary amines have one advantage over primary amines for their low binding energy with CO₂ which helps faster desorption [4].

Chapter 5 Characterization methods

5.1 Gas sorption

The gas sorption of CO₂ and N₂ have been measured for the polymers B0, B1, PDMS, B0-PDMS blend, T3 and T8 using a magnetic suspension balance (MSB) at 25⁰ C and at different pressure up to 20 bar. A software MessoPro has been used in this purpose to monitor the experiment status and result. Before each experiment the sample polymer is degassed by an evacuation step. The whole sorption experiment has been carried out by increasing pressure stepwise at some interval. The density measurement was done with helium at the start of every sorption experiment. The sorption measurement was involved with pure CO₂ and N₂. The buoyancy effect has been measured by the density of the gas environment at different pressure. However, the density was measured by thermodynamic equation of state. The compressibility becomes significant over 10 bar pressure. Different gases show different characteristics at different temperatures and pressures. That is why the temperature and pressure of CO₂ and N₂ have been normalized by their critical temperature and pressure which can be termed as reduced pressure and temperature. The compressibility factor has been calculated from generalized compressibility chart attached in **Appendix F**. The gas concentration in the polymer (cm³ (STP)/ cm³ polymer) at different pressure has been plotted and the sorption behaviour of the polymer was examined.

5.2 Density measurement

The density measurement has been carried out for the purpose of sorption measurement. A Rubotherm magnetic suspension balance (MSB) has been used to measure the buoyancy (for density) which can mathematically be written as,

$$B=\rho.V \tag{5.2.1}$$

Where V is the volume of the body and ρ is the density of the gas phase. Usually, the sample to be measured for density is reactivated by flushing with Helium and heating at 60⁰C. A vacuum pump is used for the evacuation of the gas. After the reactivation the sample is ready for the measurement. The whole reactivation process is to

measure the mass of the sample container of the magnetic suspension balance (MSB) with sample.

The mass of the reactivated sample can be determined by simply subtracting the mass of the sample container without sample (calculated by a blank measurement before) from the mass of the container with sample.

The density of the gas phase has been calculated by the pressure and temperature used in the measurement and putting them in a thermal equation of state-

$$\rho = P \cdot M / Z \cdot R \cdot T \quad (5.2.2)$$

Where P and T are the pressure (bar) and temperature (K), M is the molecular weight, Z is the compressibility and R is the gas constant.

5.3 Magnetic Suspension Balance (MSB)

The magnetic suspension balance is suitable for any pure or mixed gas even liquids for gravimetric measurement. It is possible with modern MSB to work at temperature 77 to 700 K and pressure from ultra high vacuum to 500 bars. The unique resolution and accuracy of measurement (0.01 mg) has been achieved by isolating the microbalance from the measuring environment by the magnetic suspension coupling. It actually produces a piezoelectric effect (electricity due to pressure difference) and coupling and decoupling of the electromagnet at several intervals gives better accuracy in measurement for undisturbed calibration. The whole coupling and decoupling process is automatic which makes it unique. The electromagnet voltage is controlled by a control unit which eventually gives a constant vertical position for the suspended magnet and the connecting sample with it. The mass of the sample and the magnet is transmitted to the microbalance through the wall of the pressure unit [15]. The apparatus is shown in figure 5.3.1.

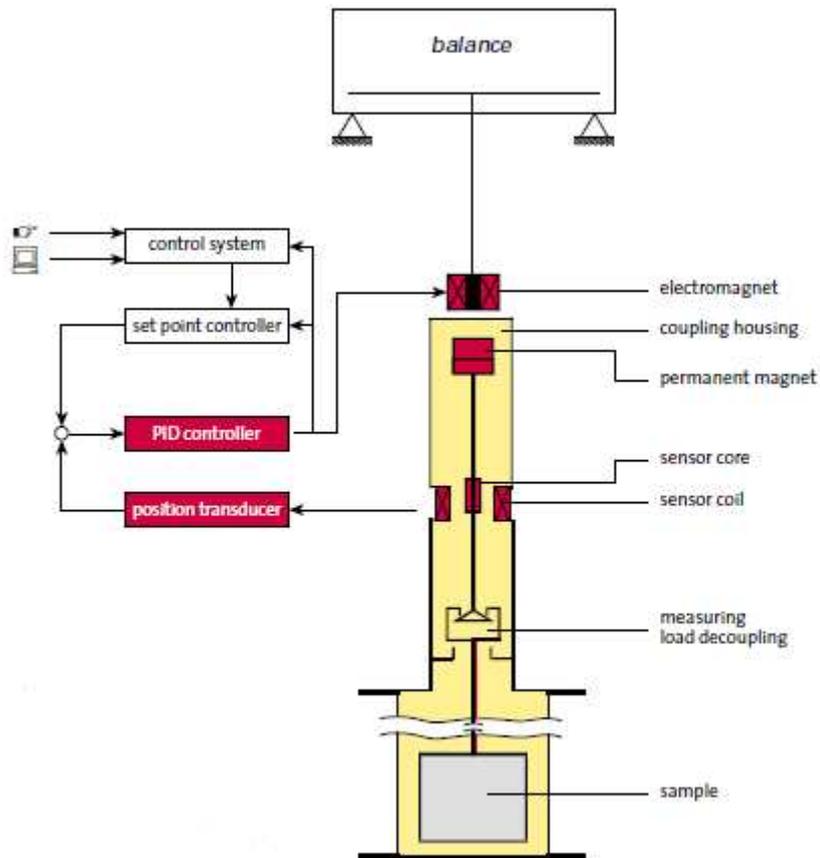


Figure 5.3.1: A complete setup of magnetic suspension balance (MSB) [15]

5.3.1 Some unique features of magnetic suspension balance (MSB)

The MSB is operated in a complete automatic way where the suspension magnet can be lowered in a second measuring position without any disturbance. The sample holder can be detached from the suspension magnet smoothly on a support. This is called the decoupling state of magnetic suspension balance. In this state the magnet suspends quite freely which is called zero position. Only the magnet is weighed in this position. The magnet can again connect with the sample container at a measuring point position. Thus, the coupling and decoupling together give very accurate measurement [15]. The whole coupling and decoupling process is shown in figure 5.3.2.

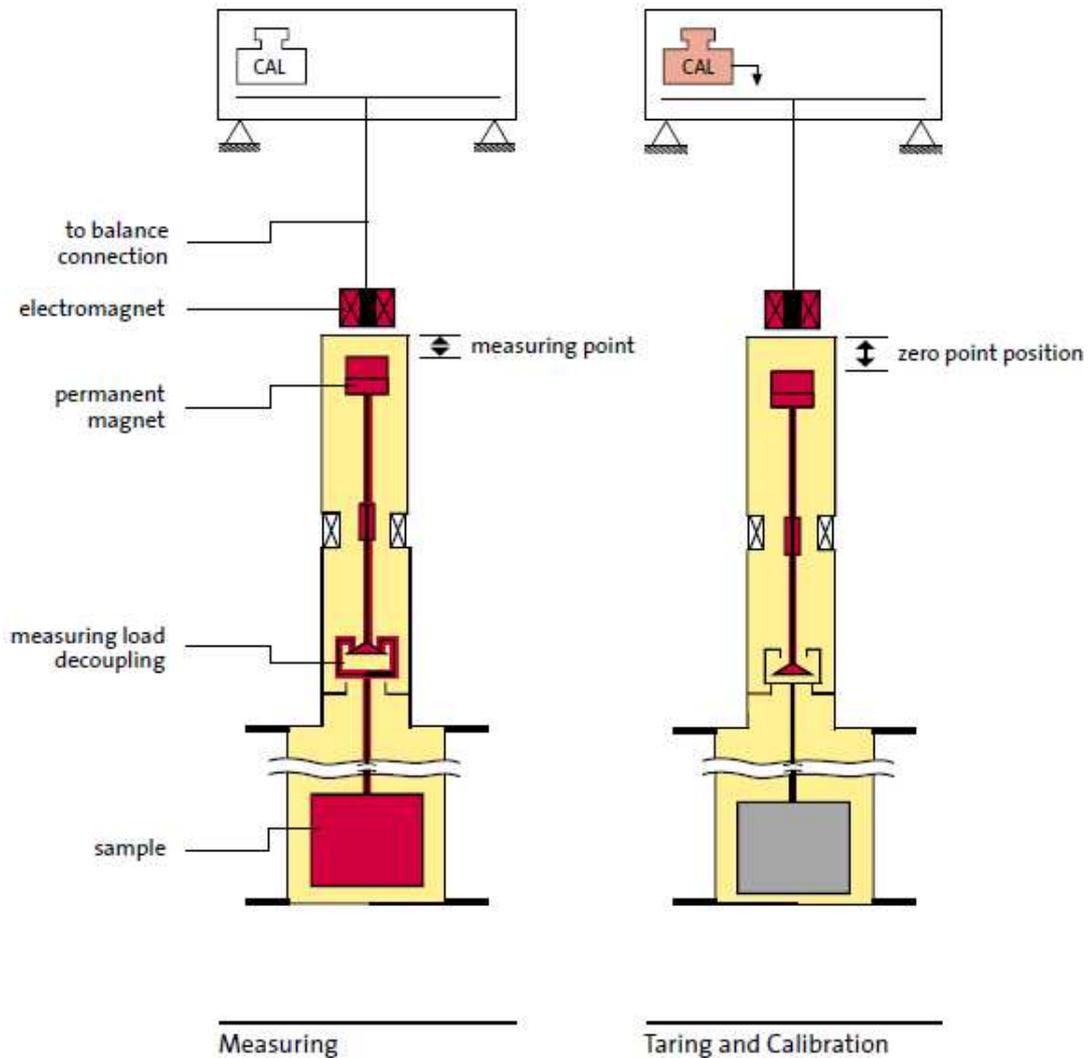


Figure 5.3.2: Automatic calibration and taring of magnetic suspension balance (MSB) [15]

5.3.2 Application of magnetic suspension balance (MSB)

Magnetic suspension balance (MSB) is a versatile apparatus which can be used in lot of experimental measurement. However, the main three applications of MSB are:

1. Sorption measurement for material transport measurement
2. Thermogravimetrics for the chemical reaction investigation
3. Density measurement for measuring the state quantities of fluids

In sorption measurement the data are recorded continuously with software like MessPro. These data can be transferred into spreadsheet programme for further evaluation [15].

For the purpose of gas permeation, the module set up is very important as it may be a source of leakage if not properly done. The polymeric membrane whose permeability will be tested is placed on a support and then put on the membrane module. The main purpose of the support is to offset the height from the lower flange of the module so that the membrane does not crack during experiment. A schematic representation of the membrane module has been shown below:

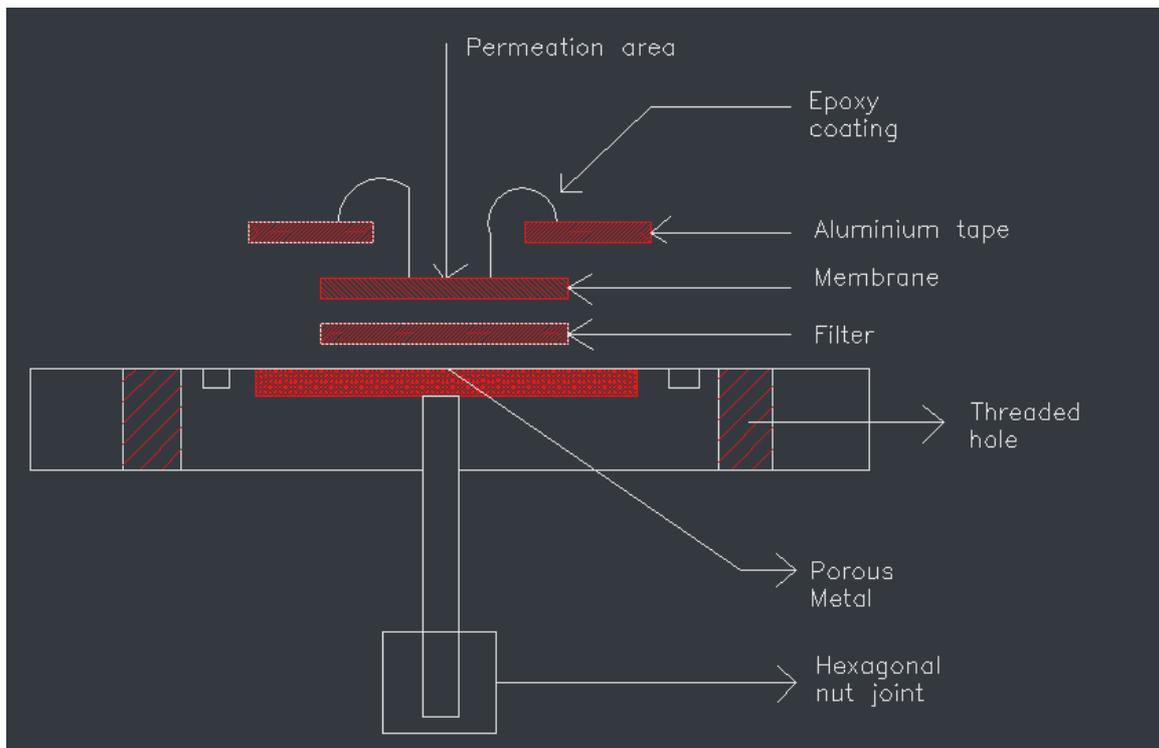


Figure 5.4.2: Cross section of the membrane module (lower flange).

The cross section of the membrane module shows that the edge of the membrane together with the support is sealed with epoxy and impermeable aluminum tape. Thus an effective membrane area for permeation is obtained whose diameter has been calculated for permeability measurement.

The permeation set up shown in figure is used to measure permeability by the time lag method. The pressure gradient (dp/dt) measurement by the transducer on the permeate side directly depends on the change of moles, dn/dt (number of moles entering in the permeate side) [18]. Considering ideal gas law, it can be stated as;

$$\frac{dn}{dt} = \frac{V}{RT} \frac{dp}{dt} \quad (5.4.1)$$

Again, at standard temperature and pressure (1 bar and 0°C) the permeate side volume change can be written as,

$$\frac{dV_{std}}{dt} = \frac{T_{std}R}{P_{std}} \frac{dn}{dt} \quad (5.4.2)$$

Where subscript std represents the standard conditions.

The flux through the effective permeation area of the membrane is,

$$J = \frac{Q}{A} = \frac{dV_{std}}{dt} \frac{1}{A} \quad (5.4.3)$$

Where Q and A represent volumetric flow rate and the effective membrane area.

In the driving force (pressure difference, Δp) term the flux can be written as,

$$J = \frac{P}{l} \Delta p \quad (5.4.4)$$

P and l represents the Permeability and membrane thickness respectively. The ratio of the P/l is often termed as permeance [$\text{m}^3(\text{STP})/(\text{m}^2\text{bar h})$].

Combining equation (5.4.1),(5.4.2),(5.4.3) and (5.4.4) gives,

$$\frac{P}{l} = \frac{1}{A} \frac{VT_{std}}{TP_{std}\Delta p} \frac{dp}{dt} \quad (5.4.5)$$

The above equation is used for permeability calculation. In real gas behaviour, the fugacity can be used instead of pressure. However, in that case compressibility, Z has to be calculated from thermodynamic equation or chart [18].

Chapter 6 Experimental

6.1 Polymer synthesis

Some of the polymers used for gas sorption and gas permeation are synthesized by changing the molar proportion of PDMS (Poly(dimethylsiloxane)) and PEG-Me (trimethylolpropane tris [poly(propylene glycol)]). The PEG-Me has been used as reticulent. The linking between trialdehyde with PDMS and PeG-Me are established by imine bond. The B1 polymer falls in this category. However, T3 and T8 are synthesized with histamine while a reaction between trialdehyde and triamine (T3) and trialdehyde and poly PEG (T8) give a characteristic difference. The B0 is synthesized without histamine with aldehyde and triamine.

6.2 Membrane fabrication

The B1 polymer is synthesized at 70-75⁰C and is kept in chloroform for 10-18 hour which gives a whitish transparent liquid. The imine bond is established by the connection between aldehyde and amine by polycondensation [16].

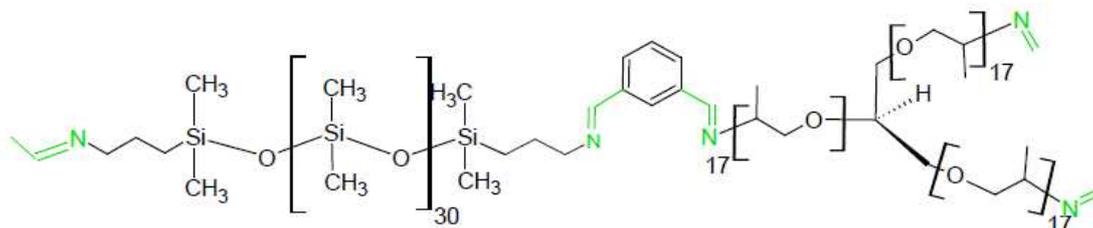


Figure 6.2.1: The connection between PDMS, tri aldehyde and PEG-Me are established by imine bond [16].

The reactions involving in synthesizing the polymer B0,B1, T3 and T8 are shown below:

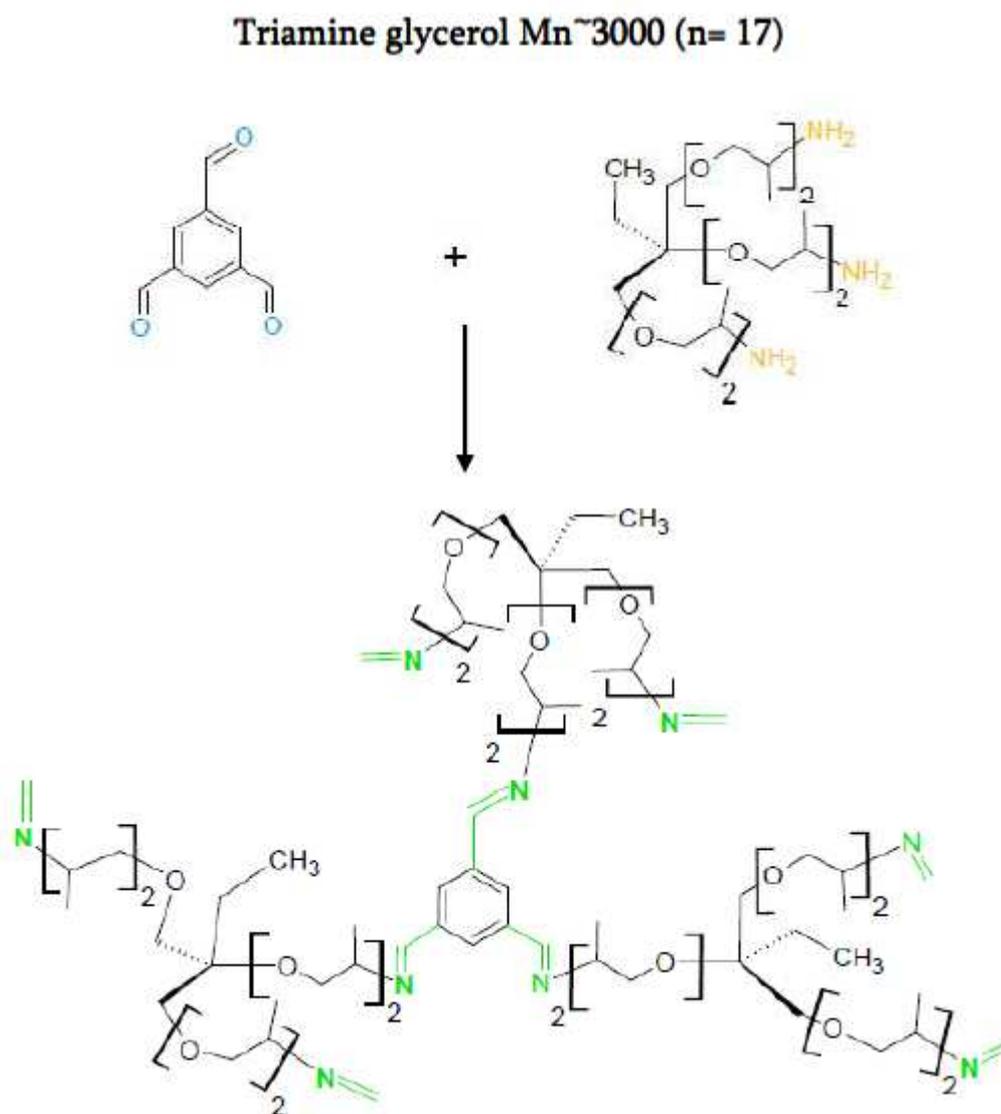


Figure 6.2.2: B0 polymer synthesis reaction [16]

Triamine Ethyl Glycerol Mn ~ 440 (n= 2)

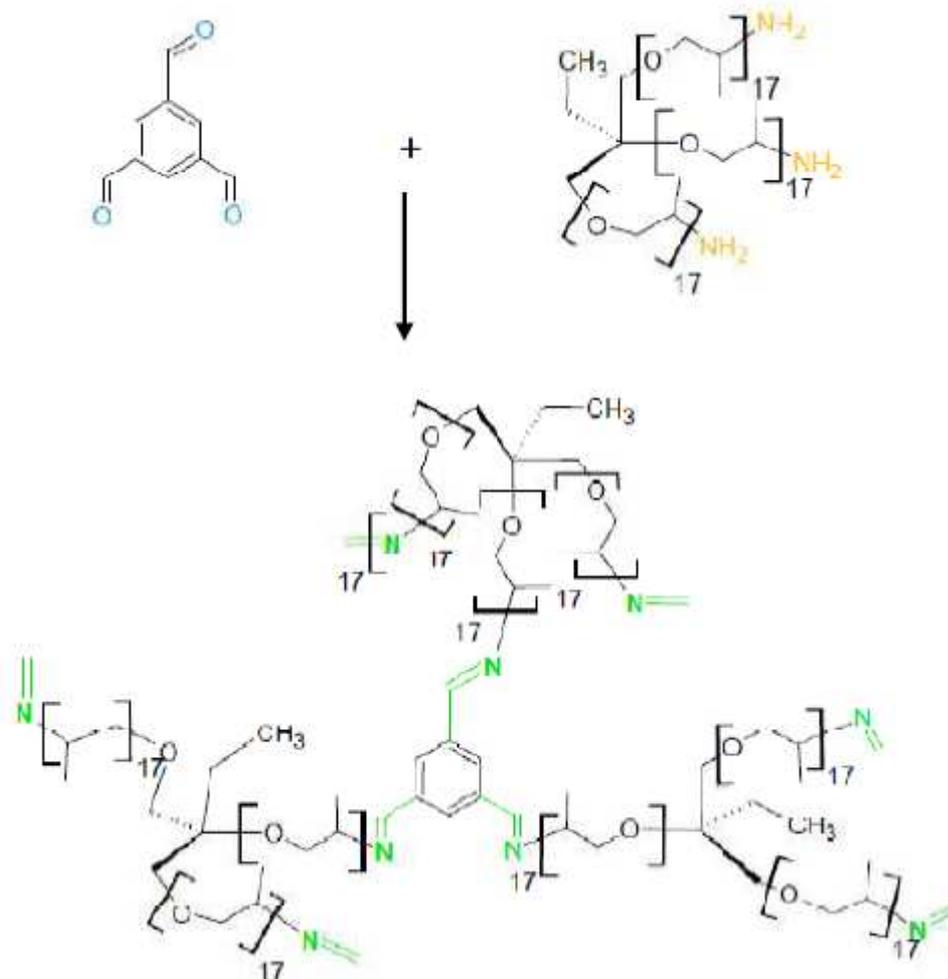


Figure 6.2.3: B1 polymer synthesis reaction [16]

The composition of B1 is 0 % of poly(dimethylsiloxane), bis (3aminopropyl) terminated and 100 % of trimethylolpropane tris [poly(propylene glycol), amine terminated] ether [16].

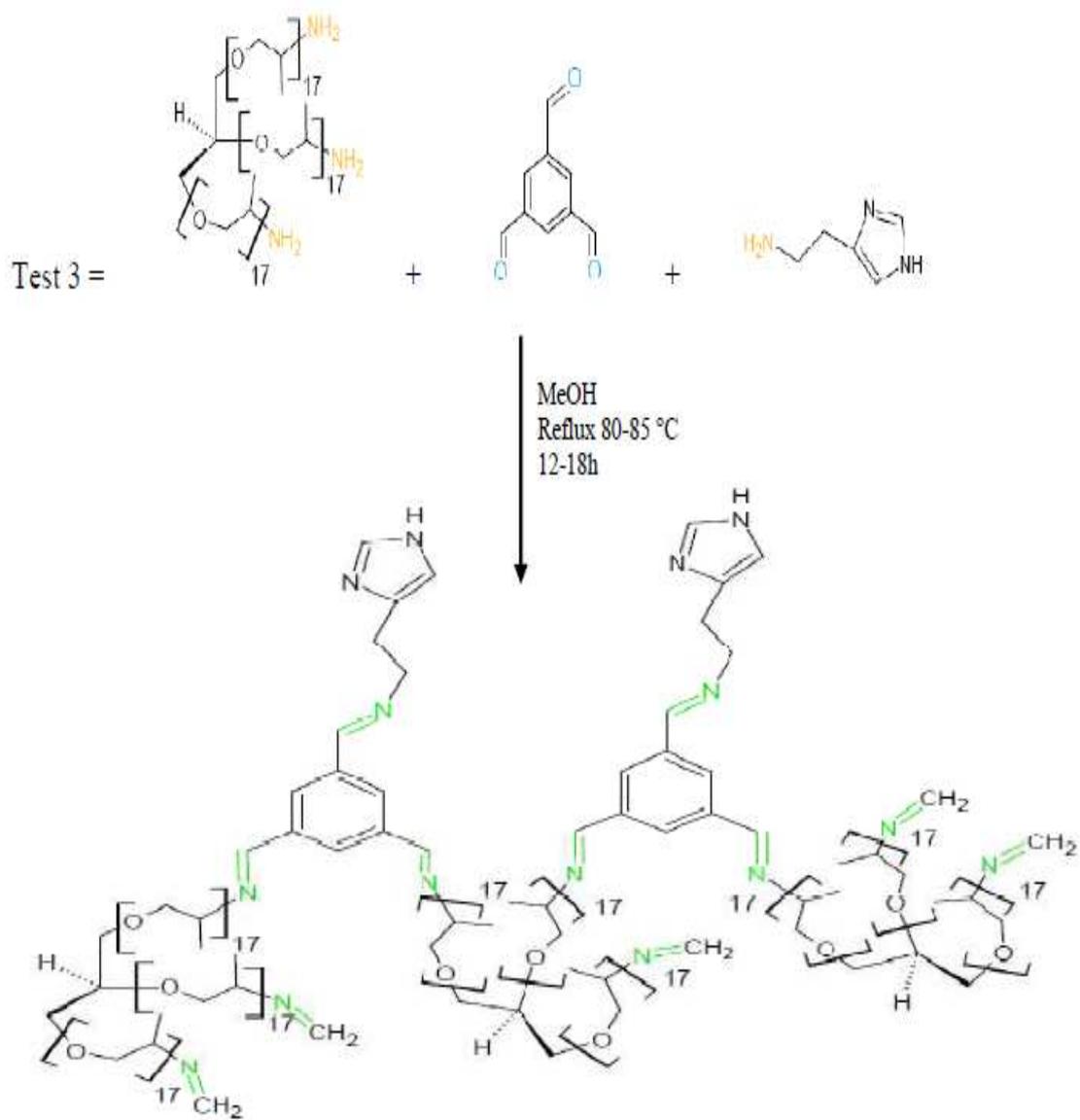


Figure 6.2.4: T3 polymer synthesis reaction [16].

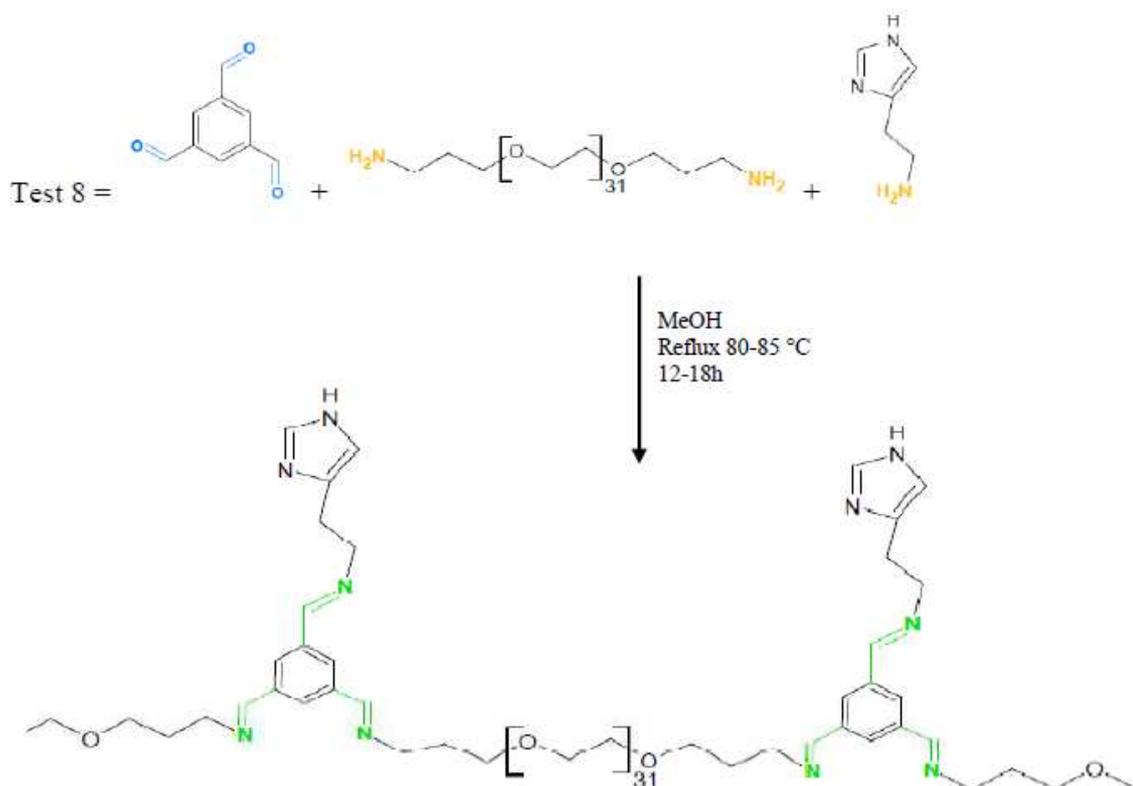


Figure 6.2.5: T8 polymer synthesis reaction [16]

All these polymers are copolymer of triamine and aldehyde or PDMS. That is why; it is assumed that they have both glassy and rubbery properties which will make them versatile. However, the inconsistency of the property may affect the durability of the polymers. As they are copolymers of both rubbery and glassy polymers, hence the glass transition temperature, T_g will be misleading if only measured by a thermal process like DSC (Differential Scanning Calorimetry). Because, a copolymer especially linear copolymer is different from a blend as the mixing is not thermodynamically favoured. That is why; a thermo-mechanical analysis is also necessary (TMA) to characterize them.

6.3 Results and discussions

A non-linear increase in N₂ and CO₂ concentration in polymers as a function of pressure was observed in the sorption measurement. The pressure was ranging from 0.5 to 20 bars. The experimental results for different solubility in different polymers for pure CO₂ and N₂ are shown here. The logarithmic line is the trend line.

N₂ solubility:

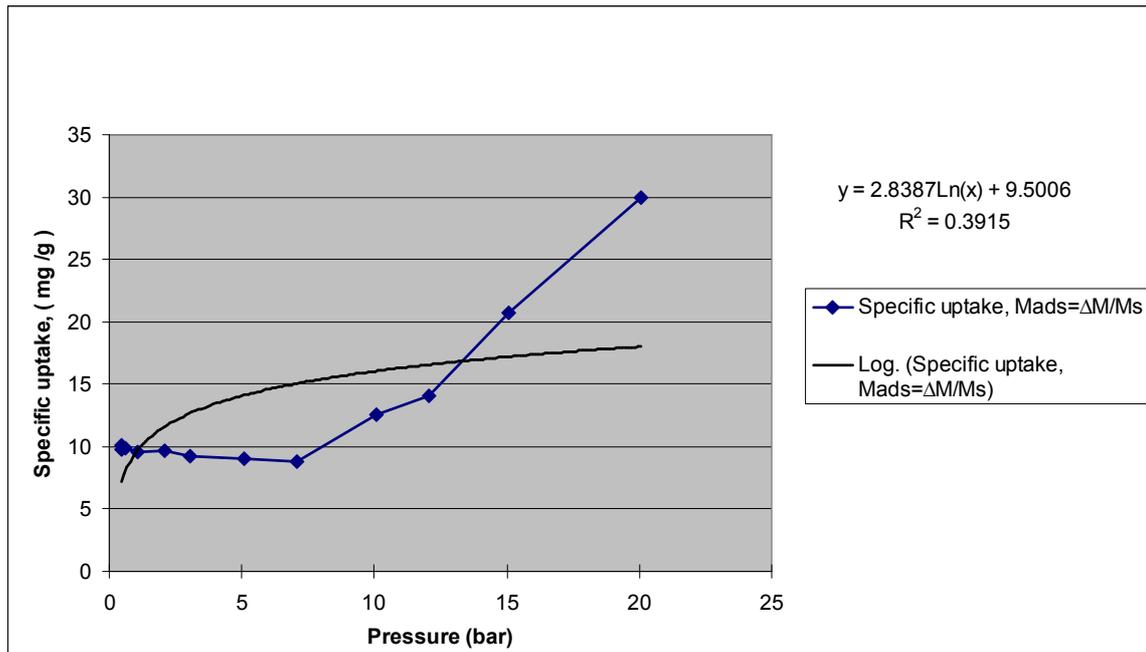


Figure 6.3.1: Specific uptake of N₂ as a function of pressure at 25⁰C in B0.

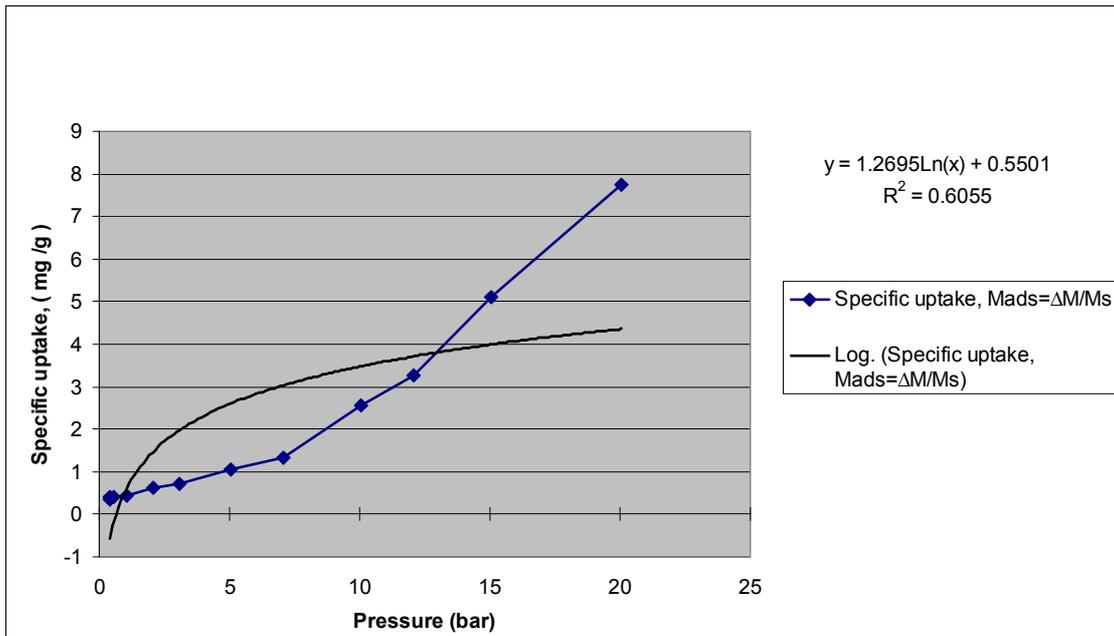


Figure 6.3.2: Specific uptake of N₂ as a function of pressure at 25⁰C in B0-PDMS (50-50 %).

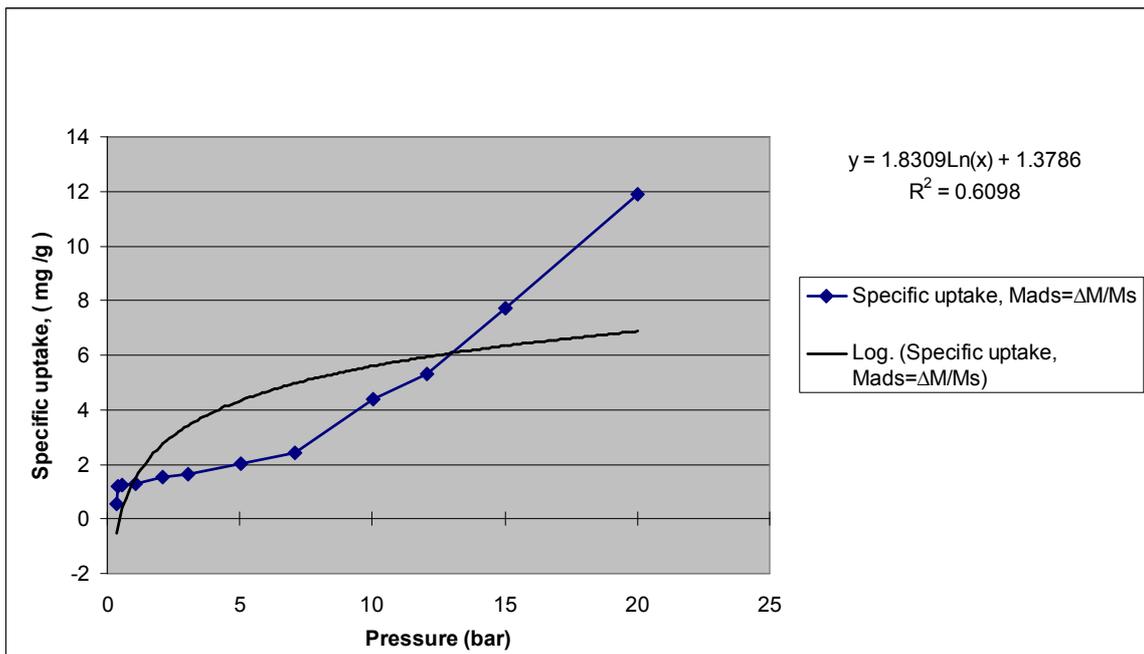


Figure 6.3.3: Specific uptake of N₂ as a function of pressure at 25⁰C in PDMS

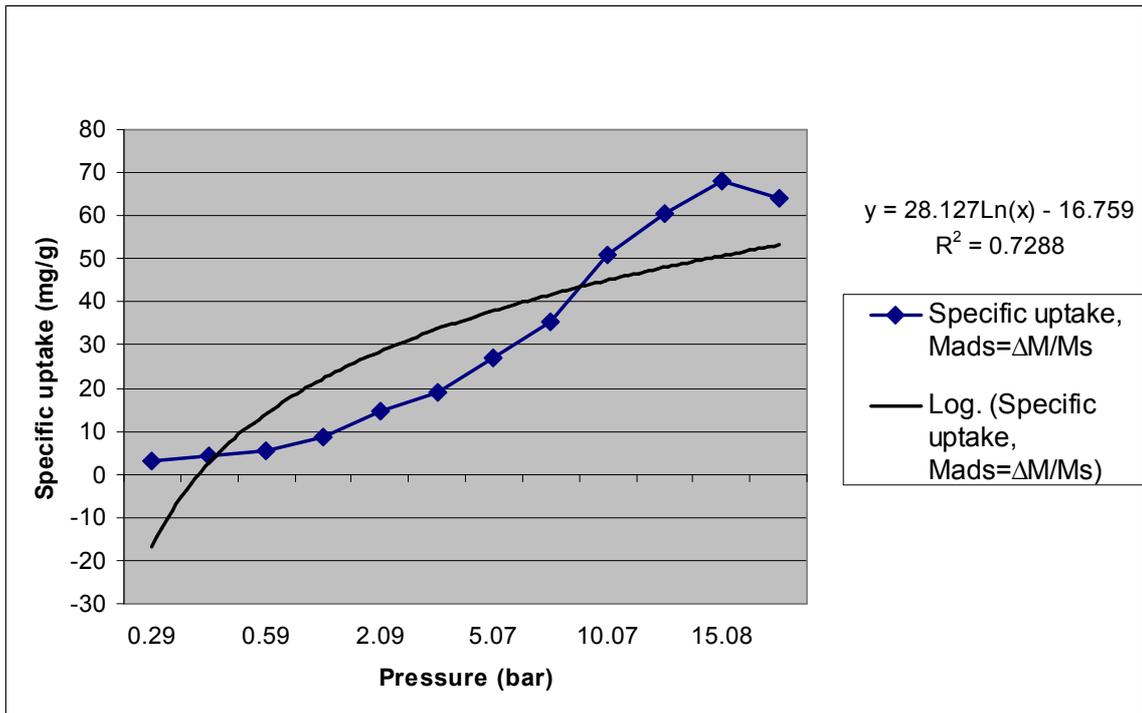


Figure 6.3.4: Specific uptake of N₂ as a function of pressure at 25⁰C in B1

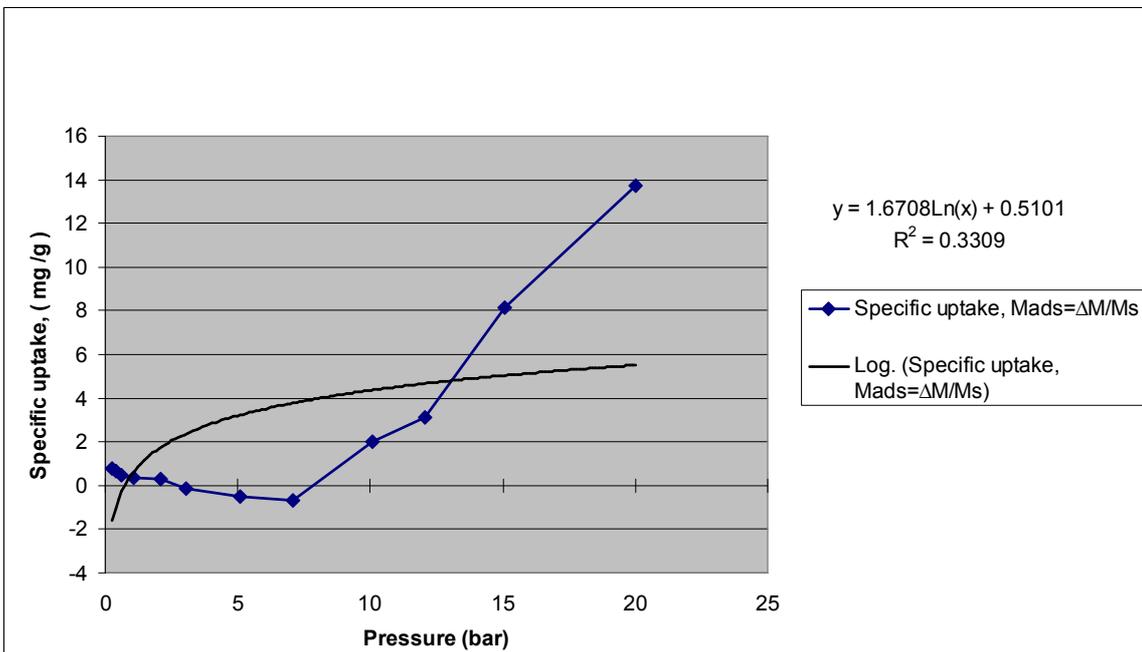


Figure 6.3.5: Specific uptake of N₂ as a function of pressure at 25⁰C in T3

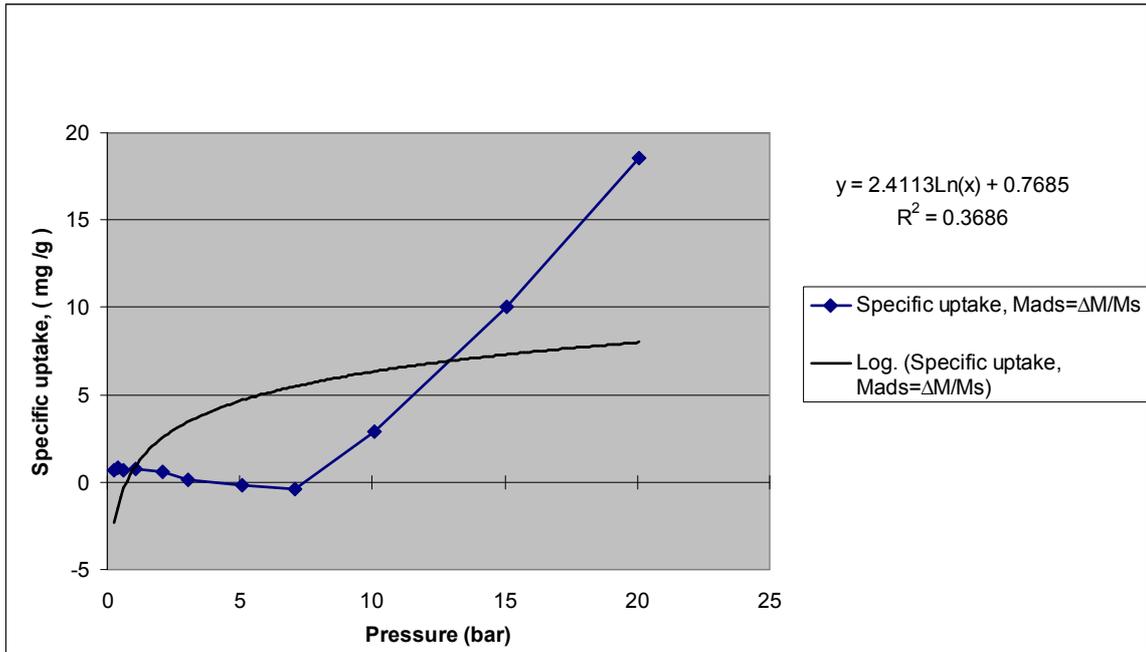


Figure 6.3.6: Specific uptake of N₂ as a function of pressure at 25⁰C in T8

CO₂ solubility

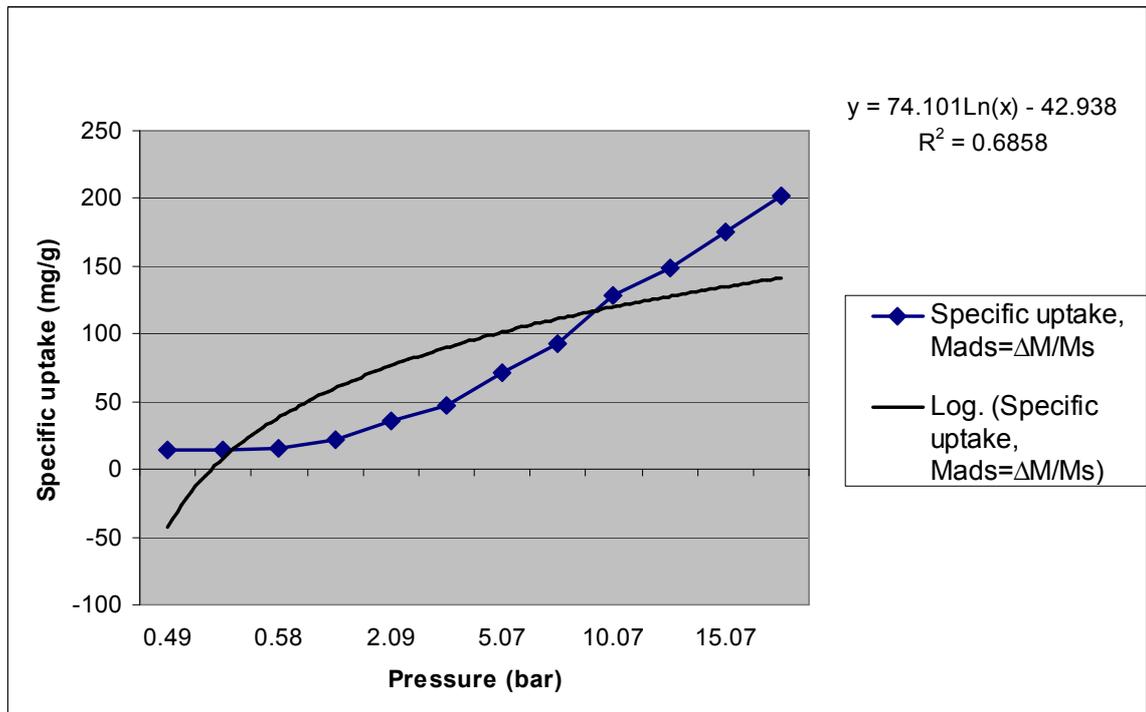


Figure 6.3.7: Specific uptake of CO₂ as a function of pressure at 25⁰C in B0

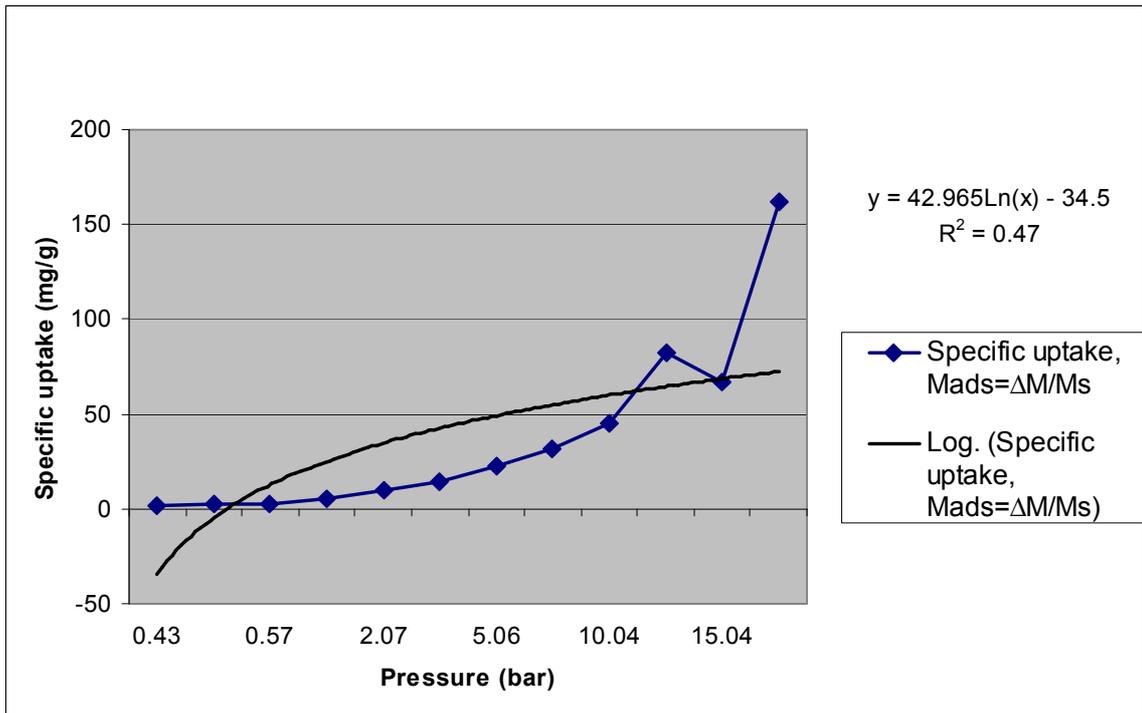


Figure 6.3.8: Specific uptake of CO₂ as a function of pressure at 25⁰C in B0-PDMS

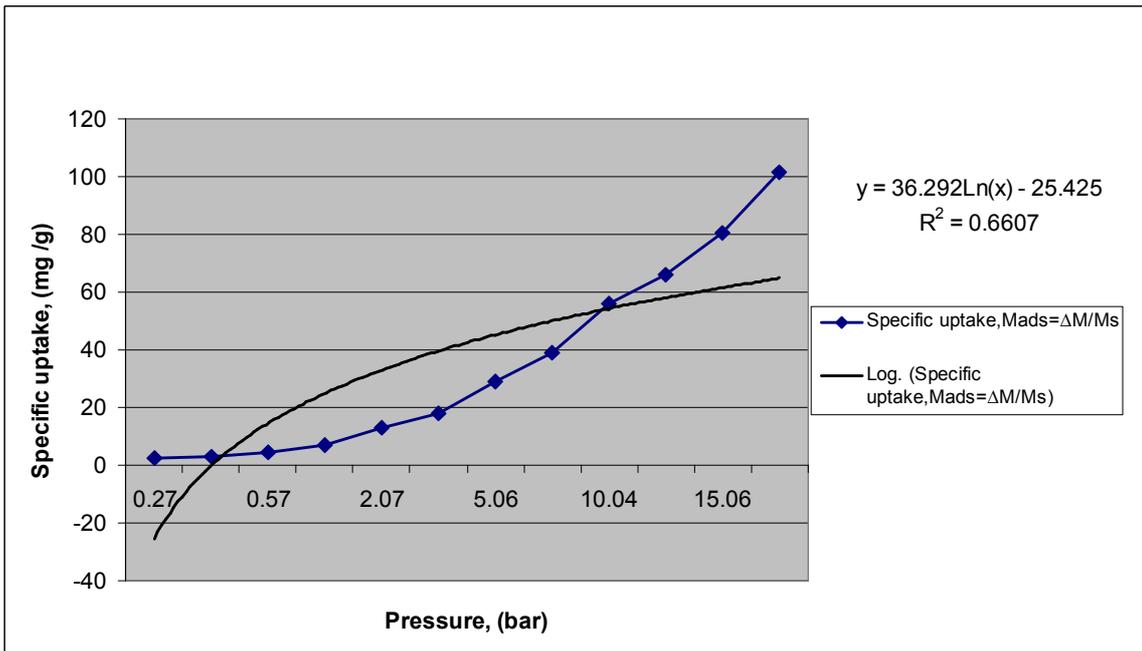


Figure 6.3.9: Specific uptake of CO₂ as a function of pressure at 25⁰C in PDMS

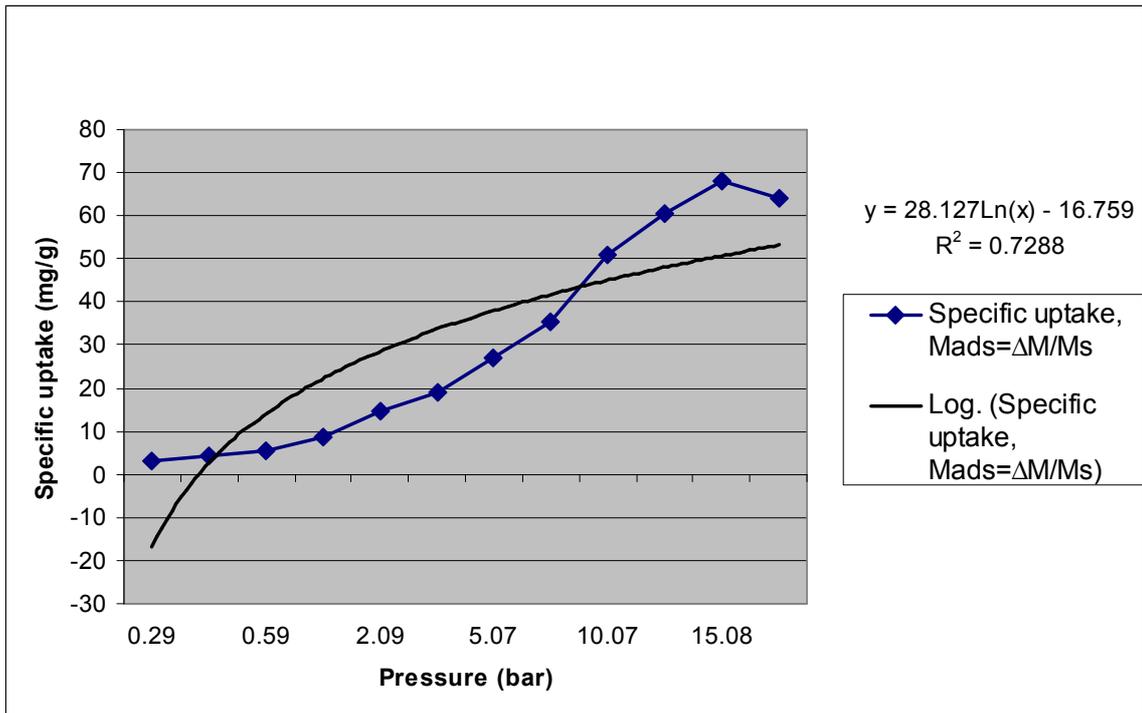


Figure 6.3.10: Specific uptake of CO₂ as a function of pressure at 25°C in B1

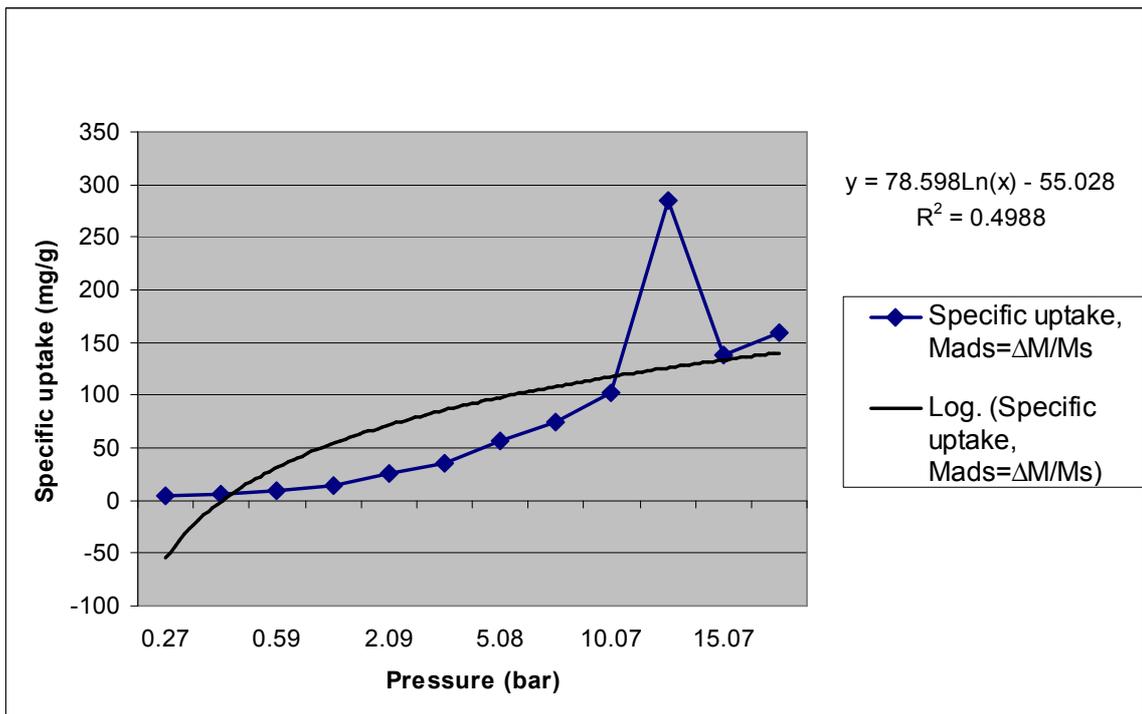


Figure 6.3.11: Specific uptake of CO₂ as a function of pressure at 25°C in T3

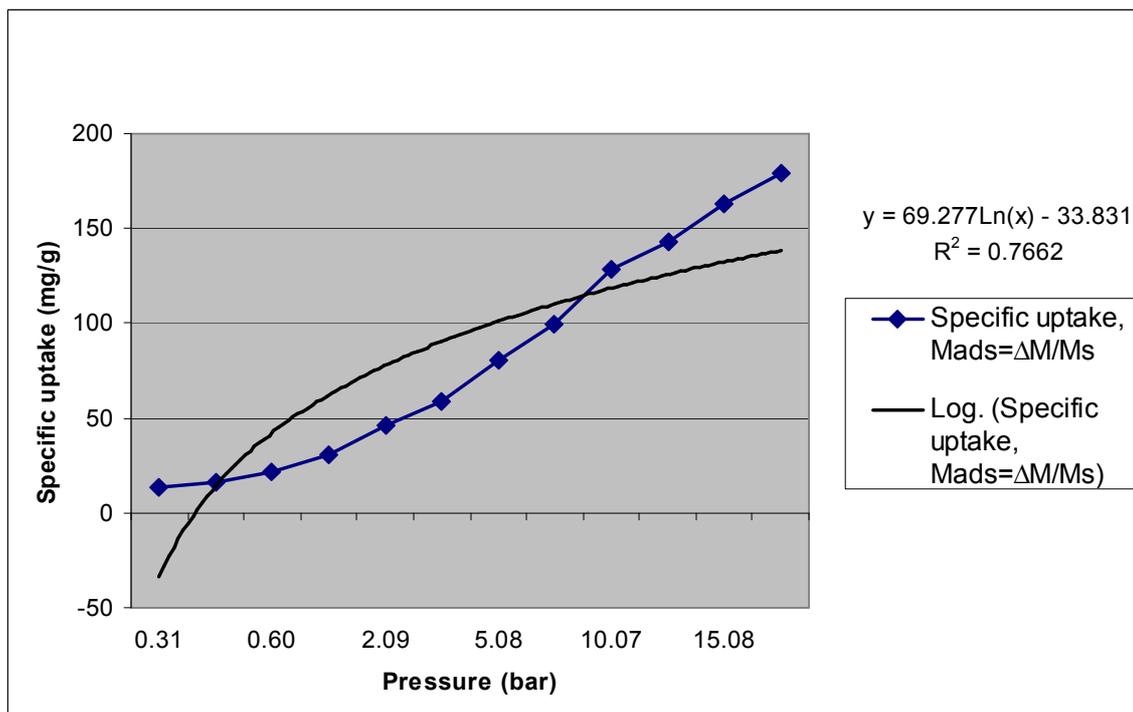


Figure 6.3.12: Specific uptake of CO₂ as a function of pressure at 25⁰C in T8

From the graphs it can be seen that, at 5 bar both CO₂ and N₂ show the higher sorption in B0 than other polymers, although CO₂ sorption is seven times higher than N₂ in B0 at this pressure. However, B0-PDMS (50-50%) and PDMS have almost same characteristics for sorption. B1, T3 and T8 show significant CO₂ sorption while N₂ solubility is very low in these polymers at 5 bar. At 20 bar pressure they also show the same pattern.

From these sorption data, the solubility of B1, T3 and T8 has been calculated as their permeability has also been measured. The solubility has been measured by the average density of the polymer and converting the sorption (mass basis) into volume basis at STP (standard temperature and pressure). From these two data set the diffusivity has been calculated by the well known and most popular equation $P=D.S$ as already been discussed in theory in chapter 3. The diffusivity for these three membranes has been measured by time lag too. A comparison between these two methods has been made.

The single gas permeance of B1, T3 and T8 has been performed and the calculations have been shown in **Appendix B**.

The two diffusivities from time lag and from equation (2.1.1) have been plotted and the following graphs are obtained:

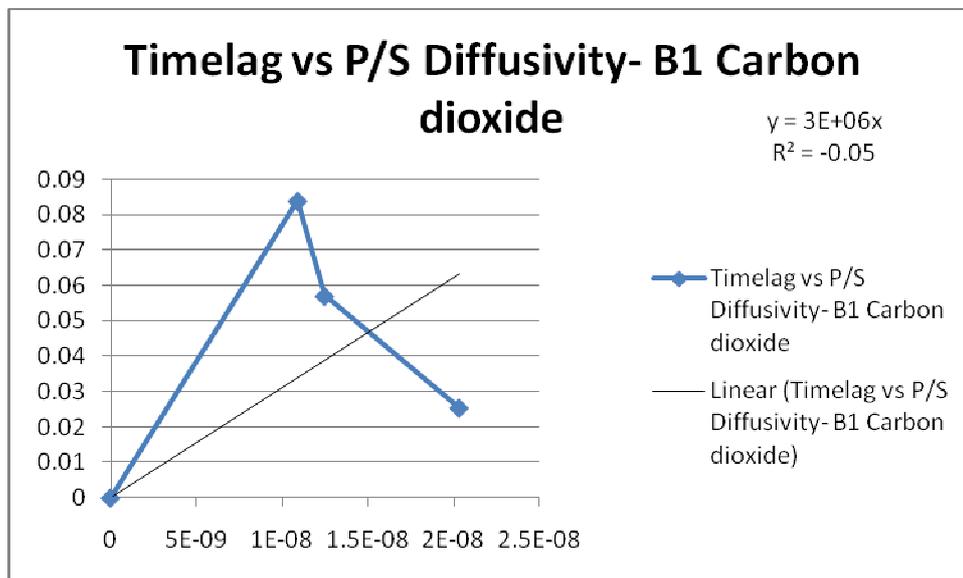


Figure 6.3.13: Comparison of the two diffusivities from time lag method and P/S (B1-CO₂)

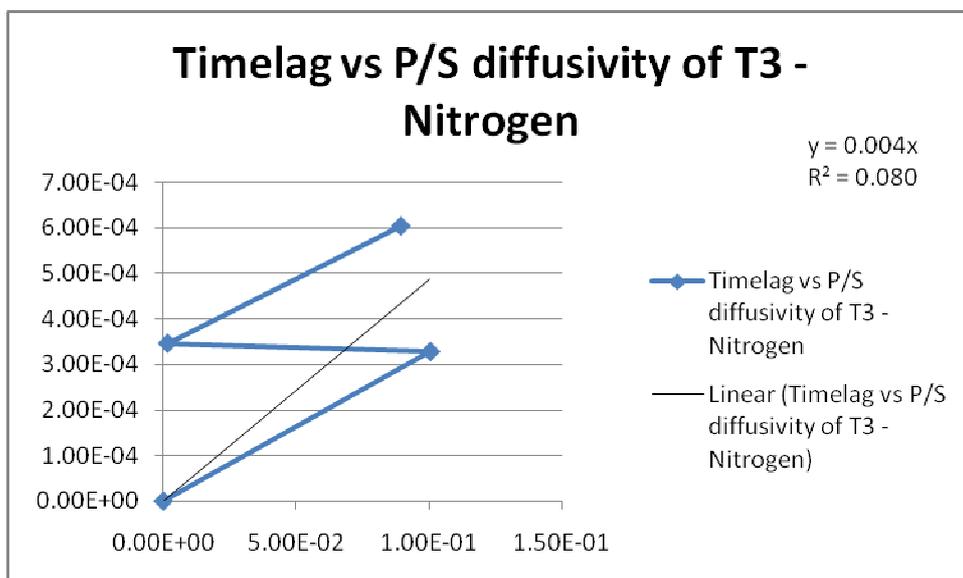


Figure 6.3.14: Comparison of the two diffusivities from time lag method and P/S (T3-N₂)

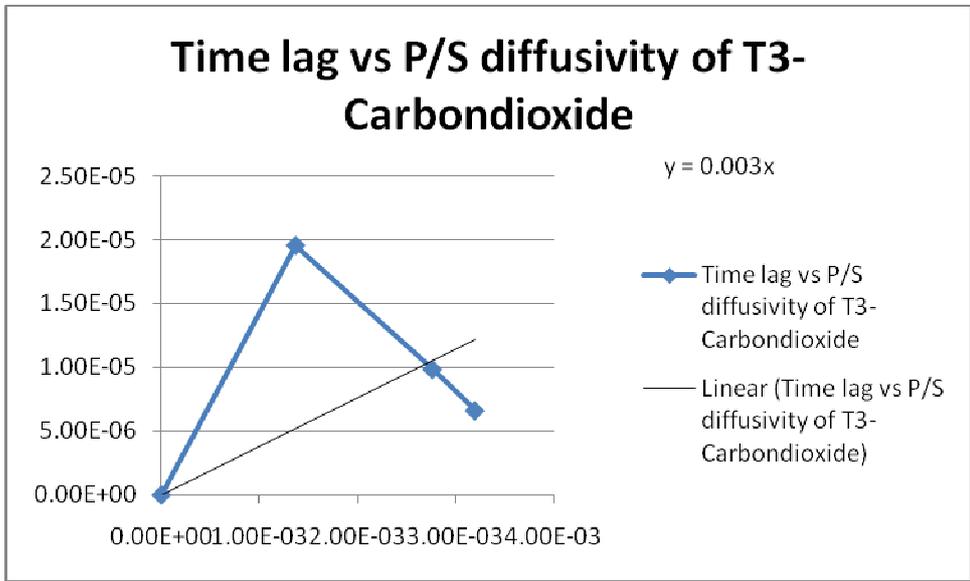


Figure 6.3.15: Comparison of the two diffusivities from time lag method and P/S (T3-CO₂)

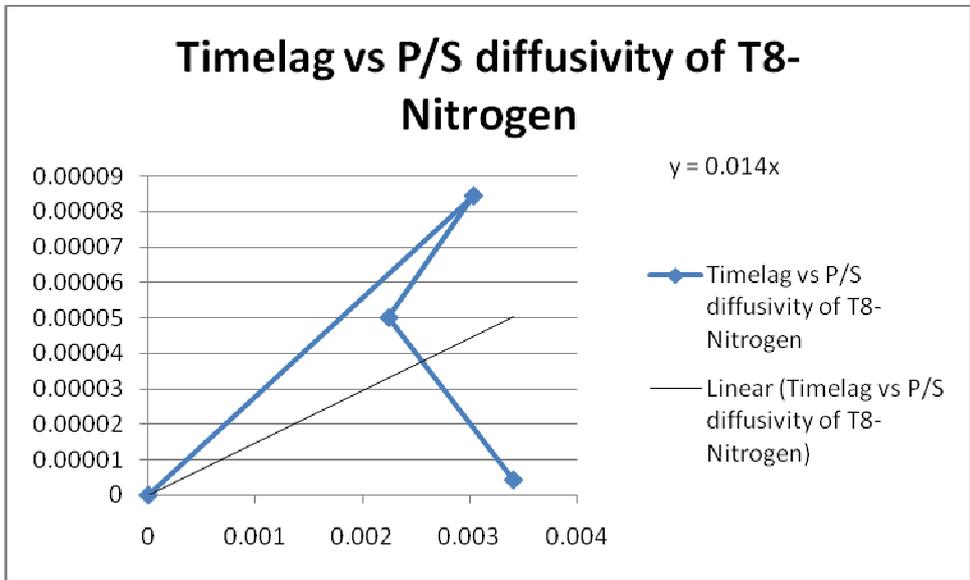


Figure 6.3.16: Comparison of the two diffusivities from time lag method and P/S (T8-N₂)

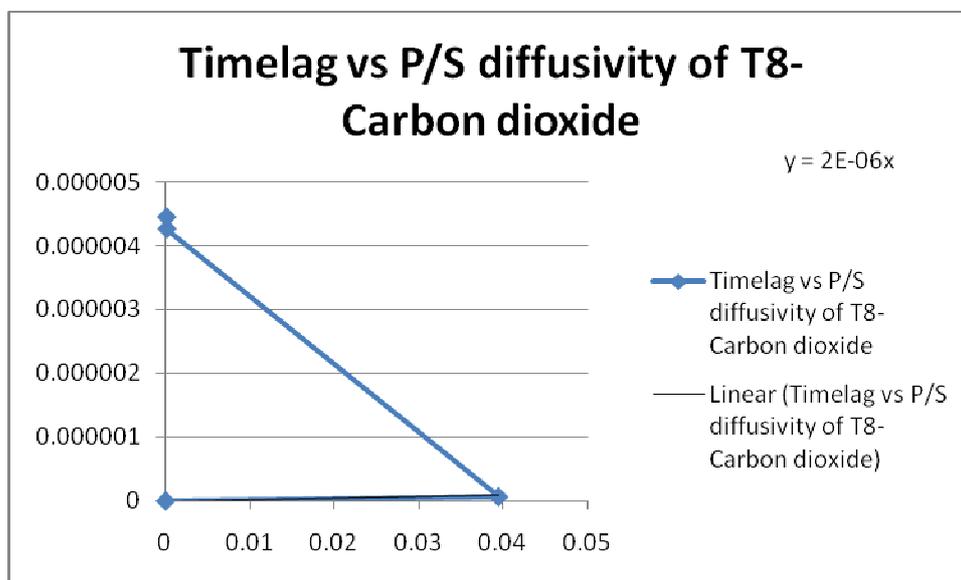


Figure 6.3.17: Comparison of the two diffusivities from time lag method and P/S (T8-CO₂)

The comparison of the two diffusivities should be $Y=X$. However, they are all completely different and do not show any particular pattern. It might be the cause for experimental error. An uncertainty analysis could be done. It can be easily estimated from the random graphs that the experimental error would be more than 5%.

Another reason for the difference in diffusivities is that the solubility has been measured in 1 bar while time lag counts the pressure on which the permeation experiment has been done.

Table 6.3.1: Selectivity and Permeability of the B1, T3 and T8 membranes at a glance.

Membrane-B1	Permeability, cm³(STP).cm/cm²h.bar		Selectivity (CO₂/N₂)
Pressure	N₂	CO₂	
5	1.62E-09	5.85E-08	36.15
3	2.80E-08	4.13E-08	1.48
Membrane T3			
2	4.66E-05	1.41E-04	3.03
5	5.18E-05	6.32E-05	1.22
7	3.00E-05	4.02E-05	1.34
Membrane T8			
3	2.57E-06	7.26E-07	0.28
5	1.59E-06	3.93E-05	24.68
9	1.12E-06	3.29E-05	29.50

From the table it can be seen that some value of CO₂/N₂ are really low. This is because the permeation experiment has been performed without humidity. As a result, the facilitated transport of CO₂ is not enhanced. Of course, the experimental error can be another contributing factor for this low selectivity. All these experiment has been done at room temperature. Hence, the effect of the temperature cannot be judged. However, the gas permeation through B1 membrane has been done at 30⁰C and 40⁰C and the diffusivities are 8.90E-01 cm²/hr and 1.94E-01 cm²/hr for nitrogen. There is no indication from this that the diffusion is increasing with temperature.

It is really difficult to comment how the polymers are behaving. However, one important thing is to be noted that the sorption curve is non linear which indicate that the consideration of ideal situation should not be valid. As the polymers' behaviour is not very much temperature dependent and rather erratic. Hence, one guess can be

made that the interaction of these polymers with gas is strong. That is why, Flory-Huggin's thermodynamics could be appropriate for them. The non linear sorption curves of these polymers also look like Flory-Huggin's isotherm.

Chapter 7 Conclusion

The gas sorption measurement and the gas permeation experiment for polymeric membranes have been studied to characterize them. However, it would be better to do the experiments with humidity for facilitated transport. The results show that the polymer matrix interaction with the gas is non ideal. However, it is not always correct for experimental uncertainties. This study can give us an idea of the effect of polymer tailoring on solubility or sorption as well as permeability of CO₂ and N₂.

Last but not least, the environmental friendliness and the cost of the membrane which is the main purpose needs to be considered. All results have been shown with some already prepared membranes. However, the preparation of membrane is not that environmentally friendly as lots of chloroform (Ozone depleting potential 0.11) has been evaporated to the environment for the co-polymerization. In industrial scale this way of membrane preparation is not possible as large scale of chloroform evaporation is not allowed for environmental regulations. At the same time, chloroform is costly, too. That's why a pro-active thinking is also very necessary, so that it does not create another problem to solve one!

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Appendix

According to Wikipedia: “appendix means a blind-ended tube connected to the cecum (or caecum), from which it develops embryologically”. In this thesis it means a supplemental addition to a given main work... or are these really the same thing?! I wonder.

Appendix A

Risk assessment, Health and safety

--	--	--	--	--	--	--	--	--

Likelihood, e.g.:

1. Minimal
2. Low
3. High
4. Very high

Consequence, e.g.:

1. Relatively safe
2. Dangerous
3. Critical
4. Very critical

Risk value (each one to be estimated separately):

Human = Likelihood x Human Consequence
 Environmental = Likelihood x Environmental consequence
 Financial/material = Likelihood x Consequence for Economy/materiel

Potential undesirable incident/strain

Identify possible incidents and conditions that may lead to situations that pose a hazard to people, the environment and any materiel/equipment involved.

Criteria for the assessment of likelihood and consequence in relation to fieldwork

Each activity is assessed according to a worst-case scenario. Likelihood and consequence are to be assessed separately for each potential undesirable incident. Before starting on the quantification, the participants should agree what they understand by the assessment criteria:

The likelihood of something going wrong is to be assessed according to the following criteria:

- 1 **Minimal**
Once every 10 years or less
- 2 **Low**
Once a year
- 3 **High**
Once a month
- 4 **Very high**
Once a week or more often

Human consequence is to be assessed according to the following criteria:

- 1 **Relatively safe**
Injury that does not involve absence from work; insignificant health risk
- 2 **Dangerous**
Injury that involves absence from work; may produce acute sickness
- 3 **Critical**
Permanent injury; may produce serious health damage/sickness
- 4 **Very critical**

Environmental consequences are assessed according to the following criteria:

- 1 **Relatively safe**
Insignificant impact on the environment
- 2 **Dangerous**
Possibility of undesirable long term effects; some cleanup is to be expected
- 3 **Critical**
Undesirable long term effects; cleanup to be expected
- 4 **Very critical**
Damaging to living organisms; irreversible impact on the environment; cleanup must be undertaken

The unit makes its own decision as to whether opting to fill in or not consequences for economy/materiel, for example if the unit is going to use particularly valuable equipment. It is up to the individual unit to choose the assessment criteria for this column.

Risk = Likelihood x Consequence

Please calculate the risk value for "Human", "Environment" and, if chosen, "Economy/materiel", separately. For activities with a risk value of 16 or 12, or a single value of 4, safety measures (designed to both reduce the likelihood and to limit the consequences) must be documented with descriptions of measures and allocation of responsibility.

About the column "Comments/status, suggested preventative and corrective measures":

Measures can impact on both likelihood and consequences. Prioritise measures that can prevent the incident from occurring; in other words, likelihood-reducing measures are to be prioritised above greater emergency preparedness, i.e. consequence-reducing measures.

Appendix B

**Calculations of permeability, solubility
and diffusivity**

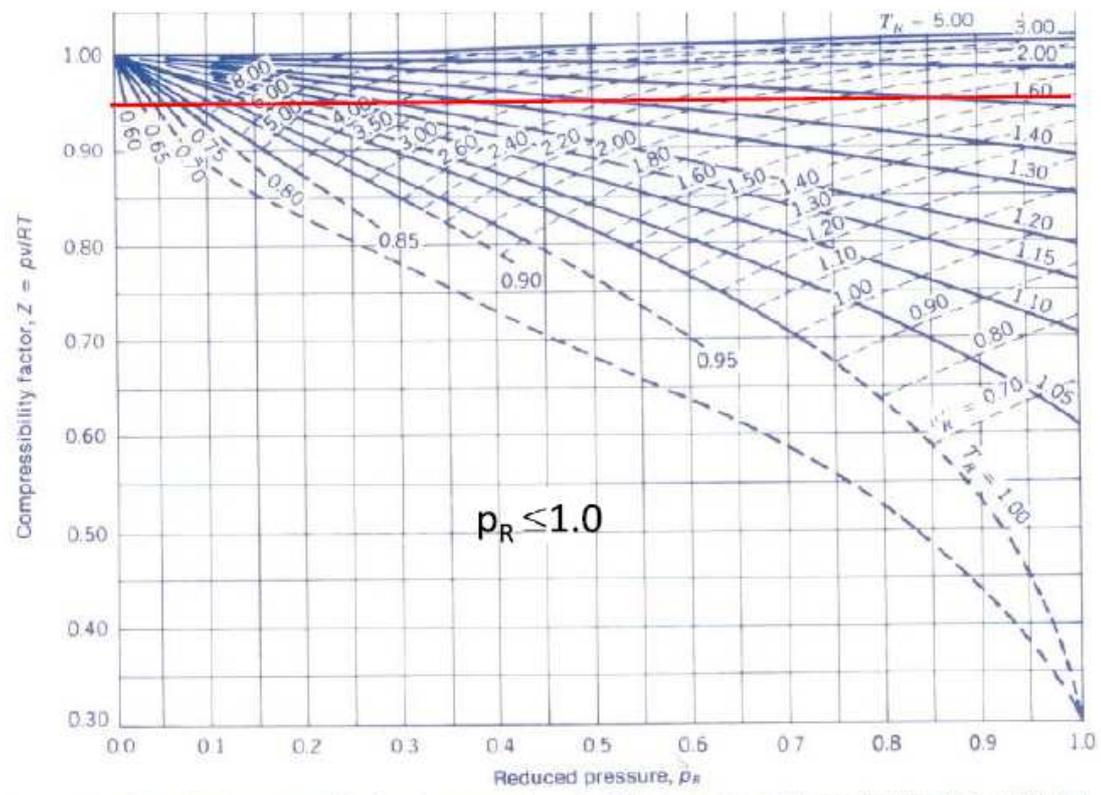
Intercept time lag.θ I²

				Diffusivity from time lag	Solubility	Diffusivity from eqn. P=D.S
0.052	2.60E+05	3.42E-04	8.90E-01	0.041236296	3.92E-08	
0.041	2.05E+04	3.42E-04	7.02E-02	0.08454722	3.31E-07	
0.052	2.60E+05	3.42E-04	8.90E-01			
0.051	5.67E+04	3.42E-04	1.94E-01			
0.052	7.43E+03	3.42E-04	2.54E-02	2.880032519	2.03E-08	
0.05	1.67E+04	3.42E-04	5.70E-02	3.311529851	1.25E-08	
0.049	2.45E+04	3.42E-04	8.39E-02	3.7469222	1.09E-08	
0.054	7.71E+03	3.42E-04	2.64E-02			
1.04E+01	2.04E+04	4.93E-04	1.00E-01	0.142137535	3.28E-04	
2.57E+01	1.81E+04	4.93E-04	8.92E-02	0.085896368	6.04E-04	
3.72E-01	3.23E+02	4.93E-04	1.59E-03	0.08664366	3.46E-04	
4.31E-01	2.78E+02	4.93E-04	1.37E-03	7.238480431	1.95E-05	
9.71E-01	5.61E+02	4.93E-04	2.77E-03	6.423848387	9.83E-06	
1.00E+00	6.49E+02	4.93E-04	3.20E-03	6.092466491	6.59E-06	
2.45E-01	1.57E+03	1.93E-04	3.03E-03	0.030436354	8.44E-05	
1.87E-01	1.16E+03	1.93E-04	2.24E-03	0.031783718	5.01E-05	
3.86E-01	1.78E+03	1.93E-04	3.41E-03	0.262037379	4.26E-06	
9.05E-01	2.05E+04	1.93E-04	3.96E-02	11.05482812	6.57E-08	
3.24E-01	8.16E+01	1.93E-04	1.58E-04	9.20092811	4.27E-06	
4.14E-01	6.91E+01	1.93E-04	1.34E-04	7.393576372	4.45E-06	

Appendix C

Generalized Compressibility Chart

Generalized Compressibility Chart



Generalized compressibility chart, $p_R \leq 1.0$. Source: E. F. Obert, *Concepts of Thermodynamics*, McGraw-Hill, New York, 1960.